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January 27-29, 1986

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Project Officer

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The U.S. Environmental Protection Agency and the American Electroplaters and Surface Finishers Society have, for several years, co-sponsored a Conference series on "Pollution Control for the Metal Finishing Industry". The Seventh of these was held in January, 1986 and this report contains the proceedings of that Conference, which dealt with regulatory status updates and presentation of multi-media research data on pollution control technologies for the metal finishing industries.

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FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water systems. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. The Clean Water Act, the Safe Drinking Water Act, and the Toxics Substances Control Act are three of the major congressional laws that provide the framework for restoring and maintaining the integrity of our Nation's water, for preserving and enhancing the water we drink, and for protecting the environment from toxic substances. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Water Engineering Research Laboratory is that component of EPA's Research and Development program concerned with preventing, treating, and managing municipal and industrial wastewater discharges; establishing practices to control and remove contaminants from drinking water and to prevent its deterioration during storage and distribution; and assessing the nature and controllability of releases of toxic substances to the air, water, and land from manufacturing processes and subsequent product uses. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

This report contains the Proceedings of the Seventh AESF/EPA Conference on Pollution Control for the Metal Finishing Industry. This cooperative forum has served both the industry and the regulatory and research communities well in the transfer of vital information relating to multi-media pollution abatement processes and strategies for the metal finishing industry, which is one of the largest industrial segments regulated by EPA.

Francis T. Mayo, Director
Water Engineering Research Laboratory

PREFACE

The Seventh EPA/AESF Conference and Exhibit on Pollution Control for the Metal Finishing Industry was held in Kissimmee, FL on January 27 - 29, 1986. This broad scope colloquium was jointly designed by the American Electroplaters and Surface Finishers Society's Environmental Committee and the U.S. Environmental Protection Agency's Manufacturing and Service Industry Branch.

The primary objective of this Conference was to continue the dialogue established at the first EPA/AESF Conference in 1978 between key members of the EPA and the metal finishing industry. The program features knowledgeable EPA representatives who explained and discussed regulatory guidelines in detail in addition to the leading industrial experts who discussed industry's efforts to effectively address the ramifications of the EPA regulations. Special sessions of the Conference were devoted to metal finishing solid waste, practical pollution control alternatives, recovery technology and emerging technologies and innovative alternatives; reports of this work appear in these proceedings.

This Conference, attended by more than 375 persons interested in the environmental problems faced by surface finishers, was considered an extraordinary success. The principal purpose of this Conference was to continue a fruitful dialogue between industry and EPA and this was achieved. The high-priority research needs of the industry were identified and solutions to pressing problems are being sought.

The proceedings are published here in order that the important material presented at this Conference can benefit as many people as possible interested in solving the intricate problems inherent in metal finishing processes. These proceedings contain the presentations made by the representatives of various EPA regulatory groups affecting the metal finishing industry, as well as presentations by parties actively addressing research and solutions to problems in this same industrial area.

The EPA and AESF are pleased to continue in this mutual endeavor which has improved communications and which should foster continued research in sound technical solutions to the environmental problems of surface finishers. The eighth Conference is planned for early 1987.

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ABSTRACT

The U.S. Environmental Protection Agency and the American Electroplaters and Surface Finishers Society have, for several years, co-sponsored a Conference series on "Pollution Control for the Metal Finishing Industry". The Seventh of these was held in January 1986 and this report contains the proceedings of that Conference, which dealt with regulatory status updates and presentation of multimedia research data on pollution control technologies for the metal finishing industries.

TABLE OF CONTENTS

A. KEYNOTE ADDRESS FOR THE 7TH AESF/EPA CONFERENCE ON POLLUTION CONTROL FOR THE METAL FINISHING INDUSTRY..........................
John H. Skinner, Director, Office of Environmental Engineering and Technology, USEPA, Washington, DC

B. CONTROL TECHNOLOGY AND THE REGULATORY PROCESS......................
Louis W. Lefke, Deputy Director, Water Engineering Research Lab., USEPA, Cincinnatti, OH

C. THE STATUS OF EFFLUENT REGULATIONS AND IMPLICATIONS OF TOXICITY REDUCTION EVALUATIONS..
Ernest P. Hall, P.E., Metals Industry Branch, USEPA - WH552

D. STATUS OF CHROMIUM AIR EMISSIONS..................................
Alfred E. Vervaert, Emission Standards and Engineering Division, Office of Air Quality Planning and Standards, Research Triangle Park, NC 27711

E. PEROXIDE-SULFURIC ETCHING: A USER'S PERSPECTIVE.....................
Kevin F. Keating, Mark A. Gouch, Multiwire East, 250 Miller Place, Hicksville, NY 11801

F. REVERSE OSMOSIS FOR INDUSTRIAL WASTE TREATMENT......................
Kevin T. Finkenbiner, Engineering Manager, C3 International, Inc., 1933 West County Road C2, Roseville, MN 55113

G. COPPER, NICKEL, AND CHROME RECOVERY IN A JOBSHOP TO ELIMINATE WASTE TREATMENT AND SLUDGE DISPOSAL................................
Tom Nadeau, G.G. Buffing and Mike Dejak, Eco-Tec Ltd., Pickering, Ontario, Canada

H. REDUCTION OF CHEMICAL USAGE THROUGH THE USE OF COMPUTERS............
Donald S. Harrison, CENTEC Corporation, Reston, VA

I. ION EXCHANGE FOR METAL RECOVERY: A DISCUSSION OF THE TRADEOFFS.......
Stanley R. Karrs, Deborah Morey Buckley, and F.A. Steward, Lancy International, Inc., Zelienople, PA

J. SLUDGE REDUCTION THROUGH USE OF THE HIGH DENSITY SLUDGE PROCESS......
M.A. Rice, CEF, Environmental Technology Division, Technology Department, Bethlehem Steel Corporation, Bethlehem, PA 18016

K. AMMONIACAL ETCHANT REGENERATION AND COPPER RECOVERY.................
Carlos Rivera, Digital Equipment Corp., Printed-Wiring Board Facility, San German, PR and Gary DeClue, Digital Equipment Corp., Technology Center, Andover, MA

L. THE USE OF RECYCLING AS A MEANS TO COMPLY WITH RCRA AND TO LOWER THE COST OF WASTE TREATMENT......................................
Phil Edelstein, Manager, ERS Division, CP Chemicals, Inc.

M. EVALUATION OF OPERATION AND MAINTENANCE MODIFICATIONS TO REDUCE TTO FROM METAL FINISHING OPERATIONS..............................
D. Wolbach and W. Buchan, Acurex Corp., 485 Clyde Ave., P.O. Box 7044. Mountain View, CA 94039 and J. Hubbard and C. Darvin, USEPA, Water Engineering Research Lab., 26 W. St. Claire St., Cincinnati, OH 45268

N. A CASE STUDY OF A MECHANICAL DRYER FOR METAL HYDROXIDE SLUDGE AT STANADYNE, INC. ....
George McRae, CEF, Moen Division, Stanadyne, Inc., Sanford, NC

O. NOVEL, SYNTHETIC COMPOUNDS FOR THE EFFICIENT REMOVAL OF NICKEL AND ZINC FROM PLATING EFFLUENT.................................
Dr. D. Brener, VP Sales and Business Development and Dr. C.W. Greer, Manager, Applications Development, DeVoe-Holbein Canada Inc., Dorval, Quebec; S.G. Nelson, President, Sanitech Inc., Twinsburg, OH

P. RECYCLING IS THE ANSWER FOR WASTEWATER TREATMENT....................
Dr. F.P. Reinhard and A.J. Grussing, Douglas America, Inc., 9701 Penn Avenue South, Minneapolis, MN 55431

Q. FINDING A SAFE ECONOMICAL METHOD FOR METAL-FINISHING SLUDGE DISPOSAL
Cynthia Harvey Draper and Raymond W. Regan, The Pennsylvania State University

R. MAGNESIUM HYDROXIDE: A UNIQUE NEUTRALIZER FOR REDUCING SLUDGE VOLUMES AND IMPROVING FILTERABILITY..............................
John Teringo, III, Dow Chemical, USA, Midland, MI 48674

S. DEVELOPING AND IMPLEMENTING AN EFFECTIVE HAZARD COMMUNICATION PROGRAM..
Barbara N. Mabbett, R.S., CHCM, Mabbett, Capaccio & Assoc., Inc., Cambridge- MA 02140

T. AIR POLLUTION CONTROL EQUIPMENT FOR SELECTED PLATING SHOP PROCESSES BASED ON EMISSION TEST RESULTS............................
William E. Powers, Naval Energy and Environmental Support Activity, Port Hueneme, CA

U. LEGAL CASE STUDIES AND COMPLIANCE STRATEGIES........................
James H. Russell, Baker & Hostetler, Cleveland, OH

V. HAZARDOUS WASTE REMEDIAL ACTION AND CASE STUDIES...................
Leon E. Lataille, Mabbett, Capaccio & Assoc., Inc., Cambridge, MA

W. COMPARATIVE STUDY OF THE USE OF PLASTIC MEDIA BLASTING FOR PAINT STRIPPING...
Charles H. Darvin, Air and Energy Engineering Research Lab., USEPA, Research Triangle Park, NC; Dean Wolbach and Cameron McDonald, Acurex Corp., Mountain View, CA 94039; Roger C. Wilmoth, Water Engineering Research Lab., USEPA, Cincinnati, OH 45268

X. HAZARDOUS WASTE RESEARCH PERTAINING TO METAL FINISHING.............
Clyde J. Dial, Alternative Technologies Div., Hazardous Waste Eng. Lab., USEPA, Cincinnati, OH 45268

KEYNOTE ADDRESS FOR THE 7th AESF/EPA CONFERENCE ON POLLUTION CONTROL FOR THE METAL FINISHING INDUSTRY

John H. Skinner
Director, Office of Environmental Engineering and Technology
U.S. Environmental Protection Agency

I have been fortunate to address this Conference now for the third year in a row and although I confess I can't remember all the names, I do recognize many faces here today. This is one of my more pleasant duties to come to Orlando in January and meet with people for whom I've developed sincere respect.

In fact, I want to take a moment to compliment you, your organization, and this Conference. The Metal Finishing Industry is one of the largest and most diverse industrial segments regulated by EPA. The interchange between the Agency and the Metal Finishing Industry is one of the most positive and beneficial in Agency experience and has served both the Industry and EPA well, as highlighted by the past and the continuing success of this joint AESF/EPA Conference. I commend your participation and we in the Environmental Protection Agency are pleased with our association with you and with the mutual utility of these Conferences. I want to specifically thank Howard Schumacher and Art Mabett of the AESF, and Roger Wilmoth of my staff for the efforts they have extended in organizing this Conference.

When I mention that Roger is now a member of my staff allows me to explain my new role. Previously, I visited with you as Director of the Office of Solid Waste. Today, I am pleased to visit with you as Director of the Office of Environmental Engineering and Technology of the Agency's Office of Research and Development. I'm not sure if Lee Thomas wanted me to bring a different perspective to the Office of Research and Development or if Lee wanted ORD to bring a new perspective to me. In either case I am happy with the new opportunity and we have mutual exciting challenges in front of us.

In the past ten years of our association with your industry, we mutually have witnessed and in fact have influenced a gradual evolution of environmental concern and resulting regulation of your industry. This process is indeed evolutionary and is not, nor probably will it ever be, complete. EPA has matured as you have matured; in some cases we evolved together and in other ways our evolution has been independent. Initially, our interface with you was by specific media (water, air, and solid waste). Your first encounters were water-related with the development and implementation of the effluent guidelines, either as a direct discharger or as an indirect discharger under the pre-treatment program. The Water Pollution Control Act of 1977 established the BPT (Best Practical Technology) and BAT (Best Available Technology) process, defining technology-based standards in lieu of water quality limits often previously imposed by states. These regulations have been promulgated for both the electroplating and metal finishing categories, and are based upon cyanide oxidation, chromium reduction, neutralization, and precipitation as BAT technologies. In fact, the final pre-treatment compliance date is February 15th. Although the struggle was arduous, these regulations are now in place and are better than they would have been without your participation in the regulatory process.

While each of you struggled to meet the water guidelines, the Agency struggled to address the hazardous waste issues. The same maturing process is occurring within the Office of Solid Waste as had occurred with the development of the effluent guidelines. This evolution of the hazardous waste regulatory program has highlighted a new set of concerns for the Nation and for you. The RCRA amendments include several new initiatives that will have significant impact on your industry. First, the disposal of hazardous waste on the land will be severely restricted, and in come cases, outrightly prohibited. Hence, your conventional means of waste disposal will be limited and you will need to pursue waste treatment, reduction, and recycling. Secondly, the delisting program has changed significantly. I know that many of you have delisting petitions pending, and some of you may have received a notice to terminate your existing temporary delistings. This means that wastes that you were previously managing as nonhazardous will now have to be managed as hazardous waste. Thirdly, the small quantity generator cutoff has been lowered from 1,000 kg/mo to 100 kg/mo. This means that some of the electroplaters who are generating small quantities of hazardous waste and were previously exempt from the Federal controls are now subject to the RCRA hazardous waste rules. Eileen Claussen will describe the status of the latest RCRA developments later this morning. In the meanwhile an additional concern has surfaced in the water area - toxicity reduction evaluations - which Ernie Hall will be discussing later. As Ernie expresses it, the water regulations could be thought of as waves. The first wave was BPT/BAT, and that is just passing. The next wave on the horizon is to incorporate discharge toxicity limits into the permitting process, which goes beyond BAT. Standardized protocols are being developed for Toxicity Reduction Evaluations, which will test for effects of pollutants which, alone or combined, exhibit unacceptably high levels of residual toxicity. The test involves bioassays using industrial discharges. The application of the toxicity-based concept is in the developmental stage at present but is anticipated to become part of many future permits. The third wave, as Ernie puts it, involves the outright ban of specific toxic chemicals. To complete the discussions, the air media activities, which are the last to be addressed for metal finishers, will be described by Al Verveart. In the air media, the major inorganic emphasis is on development of regulations for chromic acid mist, which should reach the proposal stage by mid-1988. It tentatively appears that nickel and cadmium are not candidates for regulation. Several organics will be regulated as hazardous air pollutants and NESHAP development (National Emission Standard for Hazardous Air Pollutants) is currently underway, considering most of the compounds which constitute volatile organic compounds. Under the NESHAP program, however, these will be regulated as individual compounds (for example, methylene chloride, trichloroethylene, and perchloroethylene).

The least addressed issue in this whole complex subject is that each media and the environmental control strategies involved impact the other medias. For example, treatment of metal-bearing wastewaters by hydroxide or sulfide precipitation produces sludges that may be classified as hazardous wastes.

Similarly, scrubbing of chromic acid mists produces waterborne contaminants requiring neutralization/precipitation and ultimately produces hazardous sludges. This inter-relationship between single media solutions indeed poses a challenge both to the Agency and to you.

I would like to take a few minutes to share with you some of my observations as to the directions that EPA is heading under Lee Thomas' control. I will highlight the four items I think would be of most interest to you. In his published guidance to the Agency, Lee's number one priority for FY87 is to reduce risks from exposure to toxic chemicals. We anticipate that this emphasis on toxics will be expressed in each of the media. The program will begin by a screening of chemicals for toxicity, projecting their fate in the environment, and conducting risk assessments on the most toxic candidates. An example of this approach is the recently announced program of banning the use of asbestos in certain commercial products for which substitutes now exist and gradually phasing out asbestos use in other products. His second priority is to reduce risks from hazardous waste disposal, including encouraging alternatives to land disposal. We are trying to help you in this area. As I explained earlier, you can anticipate increasing activity in this area. Invairably, you will be further restricted on disposal options and encouraged to recycle and reuse more materials now being shipped to landfills. Later this morning, Clyde Dial will describe some of our research projects that should be useful in this regard. Thirdly, Lee wants to control toxic air pollutants. Here also you can expect new activity in VOC control and chromic acid mist control and studies on additional hazardous air pollutants. Fourth, his emphasis is on strengthening water quality controls by enforcing permits and using whole effluent toxicity monitoring and limits where necessary. We do not presently know how widespread the use of toxicity reduction evaluation will be and that will be part of the upcoming/ongoing studies. We are currently developing the TRE methodology and procedures and will, over the next couple years, be studying the applications and validity of this approach. Therefore, the top four Agency priorities for FY87 address areas in which your industry has specific interest.

I realize that you are concerned with what is coming down the pike and are now asking yourselves "what are they going to do next." Philosophically, this foresight area is a traditional role of the Office of Research and Development. I must be candid in expressing that we may be facing additional cutbacks in our budgets. In addition to ongoing and planned research in these areas, the RCRA demo program, if implemented, should provide confidence for you in the abilities and limitations of specific hazardous waste treatment options.

As to my guidance to you, I feel several points have become very evident:

- Environmental controls have become a way of life and are an integral part of producing, for example, chrome-plated fixtures.
- Optimum environmental control approaches address all media impacts concurrently, i.e. we can no longer pass the problem from one media to another.
- Economic burdens of waste management can be significant.
- Probably the single most important factor to minimizing the cost of environmental management to your firm and your industry is Waste Minimization - This requires a dedication on your part to a comprehensive approach to waste generation, management, and control.
- Waste minimization coupled with Recycle/Reuse is GOOD BUSINESS.

In closing, I want to thank you - your participation in the ongoing regulatory development process has been and will continue to be essential. The Agency wants a reasonable regulatory policy - You want the same thing. Let's continue to work together to accomplish just that!

A6

CONTROL TECHNOLOGY AND THE REGULATORY PROCESS

Louis W. Lefke, Deputy Director
Water Engineering Research Laboratory
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At last year's meeting, you were introduced to a new Environmental Protection Agency organization cosponsoring this Conference--the Water Engineering Research Laboratory, one of the 15 laboratories that make up EPA's Office of Research and Development. A reorganization within the ORD laboratories brought those people you've worked with over the years into the laboratory of which I am the Deputy Director.

Because my only exposure to the area of control technology for the metal finishing industry was a paper done in college, I've been reading the proceedings of your earlier conferences and reports of work issuing from our new Industrial Waste and Toxics Control Division. From my reading, I've learned your industry is to be commended: unit processes are available and have been tried; their feasibility, practicability, and cost effectiveness have been evaluated and documented. I also know your industry is also a regulator's dream: for water, you have all the heavy metals, cyanide, greases, acids, bases; in the air are the volatile organic carbons; and for solids, you produce sludges that can be labelled hazardous.

In my office, I have an editorial-page cartoon showing a rinky-dink building in front of a large, modern building. The caption reads, "This is the building where we make the product--back there is where we do the government paperwork." Does that, in even a small way, apply to your industry?

From the earlier conference proceedings, I've learned how open the regulatory process has been. Your organization is to be congratulated for having these annual meetings, for establishing the dialogue, and for getting your knowledge into the regulatory process. Your facts and opinions are a part of it, as is the development of control technology. Whether the regulations are a mild or major burden, they are here and they are real. I, for one, am pleased that we have worked together to develop and evaluate control technology.

You are probably aware that the Office of Research and Development has no regulatory authority. We are expected to provide an objective, unbiased evaluation of emissions, discharges, and technologies (1) to assess their potential for pollution, (2) to assess the associated risk to human health and or the environment, and (3) to evaluate the technical effectiveness and cost of control technologies.

EPA promulgates two types of regulations: technology based and quality/risk/impact based. Technology-based standards are developed by studying the application of specific technologies to real-world sources. These standards consider cost, although to relative degrees between best practical technology (BPT) and best available technology (BAT). Neither BPT and BAT consider the level of the pollutant in the receiving body of water; but both are mandated by Congress to remove pollutants to levels achievable by proper use and application of the specific technology itself. Developing BPT and BAT standards requires interaction with industry, and when we at ORD are involved, we seek industry's cooperation to obtain reliable data and to ensure that the regulations are fair, reasonable, and feasible.

The second type of standard addresses impact rather than technology--it addresses risk. For example, the Agency bans the discharge of dioxin-containing materials to the environment -- period.

In evaluating a technology, we have a generic approach. First, a literature review is done to make sure we don't reinvent the wheel. Second, we do preliminary feasibility studies, if applicable, to find whether the technology is feasible or applicable to the industrial source. If step two indicates a reasonable chance of success, then laboratory-scale evaluations are done. Up to this point, contact with industry is usually minimal. Fourth in the development scheme is the pilot-plant study, which may be done at an industrial site. Lastly, full-scale evaluations are pursued--evaluations that provide real-world, real-time data with high confidence limits.

These data and information are designed to be used by EPA's regulatory offices (Office of Water, Office of Solid Waste, Office of Air and Radiation) and by industry when regulation of and, if appropriate, development of standards for an industry are considered. The regulatory offices have unique data needs that may exceed the information provided by ORD studies; thus, they typically use the ORD studies to augment their required data base when considering risk (on a national basis) and economic impact. ORD's role does not end when regulations are in force. New technologies are constantly being developed and new issues constantly need to be considered.

Again, although ORD does not make the regulations, it can and usually does influence the regulations.

Traditionally, that has been ORD's role. Unfortunately, our present budget precludes us from having as active a role as we would like. In the past we have taken a leadership role in evaluating high-risk technologies; now we must transfer much of that burden to you.

Three of the next speakers will address the status of the regulations in water, solid and hazardous wastes, and air. Although, as I said before, we've got you covered by regs, we're not out to getcha. We have jobs to do in EPA, just as you have jobs to do in your respective organizations. When we make a mistake, we expect to be told about it, and when you make a mistake, we'll tell you about it. Our goal should be the same--a cleaner environment. The regulations that have been developed so far are really no more than the rules of the game, the guidance to a cleaner environment. Control technology is the way to meet those rules.

THE STATUS OF EFFLUENT REGULATIONS AND IMPLICATIONS OF TOXICITY REDUCTION EVALUATIONS

Ernest P. Hall, P.E.
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Today I'd like to touch on what I think are the four principal points of interest from the standpoint of water regulations: the status of the Clean Water Act reauthorization; the status of the Domestic Sewage Study, which deals with water; the status of BAT for electroplating and metal finishing; and the implications of toxic monitoring, or as it sometimes is called, beyond BAT.

The Clean Water Act reauthorization was due a couple of years ago and it is in the process of happening. Last year, both the House and the Senate passed reauthorization bills; the Senate passed on S1128 June 13, and the House passed HR8 on July 23, however, the two bills are not identical and a conference committee is necessary to resolve those differences. The conferrees for this resolution have not been appointed, so there is nothing moving at this point in time.

Late last year, the House and Senate staffs had a meeting in which they were looking to identify some of the major items and they identified construction grants, FDFs, permit terms (how long), and water supply grants as among the things that were going to have to be resolved. I also understand that reauthorization of the Clean Water Act and Drinking Water Act is going to be delayed until after re-authorization of Superfund. Superfund is its own story; it is really not in the works yet. So about all I can tell you in the form of a report is, yes, I think reauthorization will happen, but no, I can't give you any timing as to when it might.

Moving to the Domestic Sewage Study, the Domestic Sewage Study is required by section 3018A of the RCRA act and it was added by the Hazardous and Solid Wastes amendments of 1984. The purpose is to evaluate the impacts of wastes introduced into publicly-owned treatment works (POTW) as a result of the Domestic Sewage Exclusion. The Domestic Sewage Exclusion basically says that if you put industrial wastes into a sewer and a sewage treatment plant treats it, neither the waste nor the solid or liquid effluent from the domestic sewer is a hazardous waste under RCRA. The Agency is supposed to make a study, findings and do some other things; if we don't, then the hammer will fall and sewage treatment plants and the wastes will become a hazardous waste under RCRA. So it becomes very critical that this report be done and that appropriate regulatory action be taken; otherwise we will all have some very interesting times. The report to Congress is due in early February and the agency work, which has been done under the Office of Water, is essentially completed. I believe that the agency's work will be completed on time to meet the reporting requirements.

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While the report is not a classified document, in the military sense, the results are not being made public until after it clears the OMB and is presented to Congress. Therefore, I don't feel free to talk very much about what the results might be. Among the things you learn very quickly, very early when you go to work in Washington, are that you never upstage Congress and you never embarrass the President. This would fall under that category. So I can simply suggest that I think it will prove very interesting reading for many of the people who are concerned with electroplating and metal finishing. I would suggest that you obtain a copy and peruse it. The Office of Water is not likely to print and distribute it because of Gramm-Rudman reductions on our printing budget. I anticipate that it will be available from NTIS in Springfield, VA and there's a possibility also that Congress may see fit to print it.

Moving on to metal finishing BAT which is the third thing I wanted to mention. BAT for electroplating and metal finishing has been a fact now for more than two years. There are no recent changes in these limitations and standards and none are planned, at least in the short term. The pretreatment standards for electroplating and metal finishing require compliance by the middle of February (1986) and in my view, this will make the regulatory picture a lot clearer and more easily understood than it has been in the past. There has been a sequence of overlapping dates and requirements which this cleans up. Unless you are an job shop plater or independent printed circuit board manfacturer who discharges into a POTW, this is the regulation that does apply and it is what you really have to meet.

We're looking at some parts of metal finishing as areas requiring some clarification or additional work. Let me go over a few of those.

One area that we're looking at is hot coatings which appears to be a bit unclear at this moment. Some hot coaters are covered in category specific regulations such as galvanizing in iron and steel; some are covered by metal finishing because there is an electroplating operation associated with the hot coating, while others are just not covered. We're looking at coming up with a coherent regulation that will clear up this regulatory sponginess.

Also, we are looking at those other things in the metal finishing area that are not now regulated, but that would be regulated if there was an electroplating operation associated with them. They are not now regulated and that is causing a lot of regulatory problems. I think that it's an area that needs to be clarified. We are also looking at two other areas that again, sometimes are covered by metal finishing but in most cases apparently are not. I'll call these machinery building and machinery rebuilding.

The timing for doing these projects is not court directed. I would suggest that hot coatings would arrive first, that machinery building and rebuilding will probably be looked at second, and that neither of them are immenent in terms of a proposed or final regulation.

Let me move on to the last but not least, of the four things I wanted to chat about with you. That is beyond BAT, or water-quality based toxics control. The Clean Water Act in 1972 established a 3-tiered scheme for regulation of water pollution and that scheme, that basic precept, has not been changed. The first level, or the base level, was to be put together based on what technology could accomplish. This looked at BAT, pretreatment standards and new source performance standards as the expressions of what technology could accomplish. Then it was to be applied universally, across the country, so that if you discharged into a big stream or a little stream or something else, there was still no difference in the minimum requirements that you must meet. The second level is water quality standards established for specific streams, water bodies and stream reaches. In this level something more might be required on a case-by-case basis when the dischargers are meeting the BAT requirements, but water quality is still being violated. A third level of control is that toxics were to be controlled, regardless of whether or not BAT and water quality standards are being complied with. It set forth three very clear tiers and it set forth a very clear direction for the agency. We feel that we are coming close to completing the major parts of the first tier, what I'll call the BAT tier (and I'm including pretreatment standards in that). The major metals regulations are now in place, with promulgation of metal molding and casting and the second part of nonferrous metals manufacturing.

The Organics regulation is projected for later this year and that will be the final major piece of the consent agreement industries, and of what we view as the really big pieces of BAT.

In the BAT round of regulation, all toxics and toxic properties are not controlled. The BAT regulations limit only selected pollutant parameters; selected toxics. If you read the development documents carefully, you will recognize that there are other toxics present that we didn't find very much of, or we felt would be adequately removed by using the technology on which the regulation was based. We tried to simplify some of the problems by reducing the number of parameters that you had to conform to. In addition, there are unregulated effluents, effluents that do not come from the BAT-regulated categories; that may, almost certainly do, contain toxics and would exhibit toxic effects. From this very brief discussion I think we clearly would conclude that the control of toxics and toxic properties is needed in this beyond BAT forum.

The agency is at this time shaping the techniques and the tools to go into and to attack this part of the problem. The starting point for beyond BAT is the water quality standard or standards that may apply to any stream reach or water body. That's obviously the starting point you must begin with when determining whether or not water quality standards are being violated, and whether or not in a particular area something beyond BAT is needed. In some cases where something beyond BAT is required, there appear to be two general approaches that might be taken. One would be a chemical-specific approach in which you would measure and control specific chemical constituents. A different approach would be the toxicity-based approach, in which the toxic properties would be measured and controls applied to reduce and mitigate the total toxic properties. There's been some interesting discussion over toxic-based controls and replacing chemical-specific controls; I would guess that in the final analysis, both will be needed and both will be used. It will not be something that is exclusive for either. Again, this needs to be and will be a case-specific analysis and case-specific determination of what needs to be done. In some cases it may be one or the other. The chemical analysis, if you're looking at a small number of discrete toxic materials, is probably cheaper and simpler. If you're looking at broad-spectrum toxicity, it very well may be that the biologic toxicity determination is easier, cheaper, and maybe more effective. The tools for measuring and controlling specific pollutants are reasonably well-developed and well-known. We've been using them and requiring them for many years, and these tools have been well-sharpened over the years. The new tools that are receiving consideration and recent press are being developed for measuring toxicity. Control methodologies to support these measurements are going to have to be developed in many cases; in some cases they are already present. The agency right now is evaluating the use of what I'll call whole-effluent toxicity.

Let me digress a minute to talk about whole effluent toxicity. I don't want to get into a hard technical discussion of how you measure whole-effluent toxicity because that's about a two-day seminar in itself. Basically, it is looking at the LD_{50} from a particular effluent, comparing it at a variety of dilutions, and evaluating its toxicity to a minimum of three receiving stream species. Then on the basis of the most sensitive of those three species, looking at hazard, at dilution in a mixing zone, and arriving at how much of this waste the stream can tolerate and still meet water quality, or conversely, how much you have to reduce the toxicity of this and other wastes to increase or improve the water quality to the point where the stream will serve the purpose for which it is classified.

At present there are toxicity measurements and reporting requirements being built into some permits across the country, I would anticipate that this number is going to increase over the next few years of permit renewels. I would also comment that this is really a first step into the use of toxic-based limits. As we have gone into other parts of this kind of program, we've had to evaluate what we've done, whether it is appropriate or not. In short, I would be surprised if a similar situation does not derive here.

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We don't know all the answers today, but we are working on them. This appears to be the next wave of regulation. I would point out to you are that all of us, will be using a new vocabulary in this effort. We will be looking at toxicity standards, looking at water quality standards, looking at mixing zones, looking at whole-effluent toxicity, looking at risk and hazard analysis, and many other things that are new in the industrial wastewater or effluent guidelines area. The implication that I would like to get across to you today is that this is in the immediate future, that it is coming, and soon. I recommend that you do take an interest in it and I will be looking forward to working with you as beyond BAT develops.

STATUS OF CHROMIUM AIR EMISSIONS

By

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Good Morning. My name is Al Vervaert. I work for the Emission Standards and Engineering Division which is within EPA's Office of Air Quality Planning and Standards, located in Research Triangle Park, N.C. Our principal function is the development of national air regulations for pollutants emitted from stationary sources.

Last year Jack Farmer, our director, had the privilege of addressing the 6th edition of this conference. At that time, he noted that an important part of EPA's standards development process is to communicate with industry to obtain your input and to keep you informed of what we are doing. In keeping with that commitment, I'm here this morning to bring you up to date with our efforts to develop air regulations for chromium emissions under Section 112 of the Clean Air Act.

As some of you may know, Section 112 is that part of the Act that authorizes EPA to control hazardous air pollutants or toxics. Specifically, it requires that EPA publish, and from time to time revise, a list of hazardous air pollutants for which it intends to establish emission standards, and to actually establish emission standards for those pollutants within a prescribed period of time.

A hazardous air pollutant, and I quote from the Act, is one "to which no ambient air quality standard is applicable and which in the judgment of the Administrator causes, or contributes to, air pollution which may reasonably be anticipated to result in an increase in mortality or an increase in serious illness." To date, seven pollutants have been listed as hazardous. They include asbestos, beryllium, mercury, vinyl chloride, benzene, radionuclides, arsenic, and coke oven emissions.

Hazardous pollutant standards under Section 112 apply to both new and existing plants and must be set at levels which, in the judgment of the Administrator, "provide an ample margin of safety to protect the public health." These standards are commonly referred to by the acronym "NESHAP" which stands for national emission standards for hazardous air pollutants. Once promulgated, that is made law, sources affected by a NESHAP may be given up to 2 years to achieve compliance.

Last year you were informed of our plan to publish a notice in the Federal Register announcing our intention to add either chromium or hexavalent chromium to the list of hazardous air pollutants. This notice was published on June 10th of last year. It states EPA's belief that there is strong evidence to support the conclusion that exposure to hexavalent compounds of chromium in air, such as chromic acid mist, causes lung cancer in people. The upper-bound, and I emphasize upper-bound, estimate of risk of cancer due to continuous exposure over a lifetime to air containing 1 ug/m^3 of hexavalent chromium is estimated by EPA to be about 1 in 100. Data available on the carcinogenicity of other forms of chromium is believed presently to be inconclusive. A final decision on the form of chromium to be listed and its actual listing will be coordinated with the proposal of regulations.

Initially, a dozen source categories were identified as potential emitters of significant quantities of chromium. These included sources that manufacture or use chromium chemicals, such as chromium electroplating, sources that burn fossil fuels, and waste incinerators. The information, however, was not adequate for most of the source categories to specify with confidence either the form of chromium being emitted or relative quantities. As a result, a 1-year program was undertaken to develop additional background information on all 12 source categories. The program was completed this past October.

Major elements of the program included for each source category: (1) the performance of emission tests at one or more representative facilities; (2) the gathering of statistical data and information on the level of control at existing plants; (3) the development of a risk assessment that estimates the public health risks associated with community exposure to hexavalent chromium emissions; and lastly (4) an evaluation of the technical feasibility of improved controls and their associated costs.

In the case of chromium electroplating, over 60 plants involved in decorative or hard chromium plating were contacted. Several plants were visited and two were selected for testing. The two plants included a job shop performing hard chromium plating of industrial rolls and a job shop performing decorative plating of automobile bumpers. The test results were used to develop emission factors which were then used to estimate nationwide emissions.

Statistical data on the industry was obtained primarily from earlier EPA reports such as the development document for the effluent limitations guidelines and pretreatment standards. Assumptions with regard to the current levels of control were based on limited information provided by several control device vendors and manufacturers of fume suppressants.

Estimates of public health risks were obtained by coupling the unit risk factor cited previously, that is the 1 in 100 figure, with estimates of population exposure. The exposure estimates were derived using model plants, emission estimates, dispersion modelling, and census data. Dispersion models are used to predict ambient concentrations of a pollutant at varying distances from an emission source. By combining these predicted concentrations with population data, the number of people exposed and their level of exposure can be estimated.

Two measures of risks were calculated. One was maximum individual risk and the other was annual incidence. Maximum individual risk refers to the probability of contracting cancer experienced by the person or persons exposed to the highest predicted concentration. Annual incidence on the other hand is a measure of the overall health impact on the entire population exposed. It is expressed in terms of number of cancer cases per year.

The control techniques evaluated included the use of add-on control devices such as mist eliminators and wet scrubbers, and the use of fume suppressants. Cost information was obtained directly from control equipment vendors and fume suppressant manufacturers.

Our findings and key assumptions, as they pertain specifically to the chromium electroplating, are as follows. There are an estimated 9,700 facilities in the U. S. that plate chromium from chromic acid baths. About 7,300 of these, or 75 percent, are believed to be hard platers and the remaining 2,400 are believed to be decorative platers. Half of the hard platers and 90 percent of the decorative platers are assumed to have controls in place. The balance are assumed to be uncontrolled.

Together, these facilities are estimated to emit over 60 tons of hexavalent chromium to the atmosphere per year. The upper-bound estimate of risks resulting from these emissions is an annual incidence of 32 lives per year and a maximum lifetime risk greater than 1 in 10,000.

Additional controls are available at what appears to be reasonable cost, although no economic analysis has been performed to confirm this. Depending on the type of additional controls implemented, risk reductions ranging from about 75 to 90 percent appear achievable.

Because of the national scope of the problem due to the large number and distribution of plants involved, the high estimated risks, and the substantial potential for improved control, the EPA has concluded that the development of a national standard or NESHAP for chromium electroplating is warranted. Work on NESHAP development began this past November. I am the EPA lead person on the project. A contractor, Midwest Research Institute (MRI), has been and will continue to work with us on the technical aspects of this project. The MRI lead person is Mr. Randy Strait. Another contractor, JACA Corporation, will be handling the economic analysis. The JACA lead person is Mr. John Gracey.

We anticipate that it will take 2 1/2 to 3 years to develop a proposed regulation. The process which we intend to follow in developing that proposal includes three principal phases. The first consists of information gathering; the second, analysis and documentation; and the third, the development of the actual standard.

We are presently in the first phase. Our emphasis right now is on locating and visiting well-controlled, representative plants, as candidates for emission testing. Emission tests will be performed at select plants to determine the performance capability of alternative control techniques. Whatever assistance that AES as an organization or you as individuals may be able to provide to us in locating and selecting plants for testing will be most appreciated.

We are also presently involved in assessing alternatives for expanding and updating the current data base. Our current data base on the number, types, and distribution of chromium plating plants is very limited and contains substantial uncertainties.

In the second phase, detailed analyses will be performed based on the best available information to reassess the existing risks and to identify feasible control options to reduce those risks. The control options identified will then be examined to determine their emission and risk reduction potential, cost and costeffectiveness, as well as the economic, energy, solid waste, and waste-water impacts that would result from their application. All this information will be compiled and presented in a background information document for proposed standards. This document will contain whatever supporting data are needed to establish the NESHAP.

The third phase, the standards development phase is the most judgmental, and perhaps the most difficult. This is the phase at which all the information gathered and analyses performed are evaluated and the difficult decisions with respect to both the applicability and stringency of the regulation are made. This activity is now commonly referred to within EPA as "risk management." Whatever decisions are made, the rationale for these decisions will be detailed in the Federal Register announcement for the proposed regulation.

In closing, let me emphasize that your participation is important to us and that we welcome any assistance or input that you can provide throughout this NESHAP development process.

This concludes my prepared statement. Thank you for your attention.

PEROXIDE-SULFURIC ETCHING: A USER'S PERSPECTIVE

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The technology behind peroxide-sulfuric etching has come a long way since the 1970's, when it was introduced as a pre-plate etch process. Today it's use as a final etchant has become increasingly common among circuit manufacturers due to the improvements in chemistry, equipment and overall cost. In addition to these incentives is the increasing environmental concerns that manufacturers can no longer afford to overlook. Peroxide-sulfuric etching addresses some of these problems that are shared by managers, workers, and local officials. In 1984, Multiwire East (located on Long Island), chose this etchant for use in a new, state of the art manufacturing plant situated where waste water restrictions are some of the tightest in the country. One never knows with certainty how well a product will work unless he actually tries it, and it is the scope of this paper to share with it's readers the advantages and disadvantages of peroxide-sulfuric etching from a user's perspective.

Why Peroxide-Sulfuric?

The chemical choices made for most of our plant's operations centered around their compatability with a waste treatment system that is relatively new to the metal finishing industry-ion exchange. In this system, rinsewaters containing chelated and unchelated copper, tin, lead, and nickel are segregated and pumped through ion-specific resin columns. In the case of copper removal, a cation resin bearing positively charged hydrogen ions is used which exchanges the ions for polyvalent copper ions, as shown in fig. 1.

The effluent, now containing an excess of H ions, are neutralized with sodium hydroxide. The water is then discharged to a municipal treatment plant.

The resin in the column eventually becomes saturated with copper ions. It now must be flushed, or "regenerated" with an appropriate solution which will "pull off" the metal ion and substitute back another hydrogen ion. In the case of unchelated copper, a dilute sulfuric acid is used. (See Fig. #2).

What one is left with is the original "recharged" cation resin and a small volume of concentrated copper sulfate solution,

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which can be re-used for plating. Nickel extraction employs the same method. The by-product in this case would be nickel sulfate. A typical cationic resin will also exchange hydrogen ions for sodium, calcium and other cations that may be present in the waste stream. Removal of these cations is usually unnecessary or undesirable for wastewater pretreatment. Many ion exchange resins are available that have chelating functional group that is highly selective for heavy metal ions. These chelating resins are similar to cationic resins in that they undergo reversible exchange between the hydrogen form and metal form. They are more cost effective for removal of heavy metals in wastewater pretreatment because their selectivity for the heavy metals allows other cations to pass through. This conserves the exchange sites to be used for the target metal cations reducing the cost per pound of metal removed.

The Multiwire East facility generates approximately 25,000 gallons per day of acidic unchelated copper bearing rinsewater including rinses from the sulfuric-peroxide etchine process. This waste stream is pH adjusted to a pH of 4 before being pumped through the ion exchange columns. The usual three column merry-go-round system is used. The waste is processed through two columns in series while the third column is out of sevice or regenerating. Each column contains 50 cubic feet of resin. The flow rate through the columns is 1 gallon per minute per cubic foot, or 50 gallons per minute. Treatment costs are approximately $0.2 per gallon treated for an influent containing 10 - 30 mg/l copper.

Multiwire engineers developed a reversible adsorption process for removal of complexed copper bearing rinse waters from an electroless plating operation. The electroless rinses are segregated from all other rinses and pumped through absorption columns We process 6,000 to 10,000 gallons per day at a cost of $.05/gallon.

The reclaimation of chelated copper, lead and tin require a more elaborate system of ion-exchange resins. The process descriptions are beyond the scope of this paper, but all share the same advantage in that all metals are 90 percent or more reclaimable. The system is automated whereby all of the valves, pH meters, pumps, etc.. are tied into a small computer. There is no sludge to deal with, no odors, and minimal chemical costs as compared to precipitation methods.

In order to examplify the efficiency of the ions exchange system, a table is shown on the following page.

PARAMETER	LIMIT mg/l	INFLUENT mg/l	EFFLUENT mg/l
Copper	2.0	10 - 30	0.1
Lead	0.1	10 - 30	0.1
Nickel	2.0	5 - 10	1.0

Ion exchange systems can be tailor-made for handling rinse water from most, if not all, of the common etchants used today. What makes peroxide-sulfuric systems attractive is the simplicity behind it: only the free copper ions in solution need be considered, and the same applies for precipitation methods as well.

In addition to rinse water, the handling of the spent etching solution is also relatively easy. Actually, the solution itself can last for an indefinite period, so long as one removes the copper. To achieve this, Multiwire uses a crystalizer and auger system which will be described in detail later in this paper. The process is continuous; there is nc sludge build-up, and the by-product is valuable copper sulfate pentahydrate crystals.

Aside from waste treatment, peroxide-sulfuric etching has another important benefit which was our primary basis for choosing the etchant, and that is it´s compatibility with all resist types, particularly aqueous photoresist. One of Multiwire´s objectives when setting up their new plant was to utilize chemistries that are both cost effective and, more importantly, safe for the worker and the environment. It was our intention to use aqueous film as the primary resist, and lead/tin for the products pattern-plated surface features. Alkaline etching requires maintaining a relatively low pH for aqueous compatibility, otherwise breakdown can result. (The author has seen fully aqueous film work well in some alkaline etchers, while severe breakdown was observed in others.) Cupric chloride etchants work well with all dry films, but they will aggressively attack lead/tin. This left us with peroxide-sulfuric as the only etchant which we could use with confidence.

The Operation

The etching process can be described in simplest terms by the following equations:

1. $Cu + H_2O_2 + H_2SO \rightarrow CuSO_4 + 2H_2O$

2. $H_2O_2 \rightarrow H_2O + 1/2\ O_2 \uparrow$

3. $CuSO_4 + 5H_2O \rightarrow CuSO_4\ 5H_2O \downarrow$

Let us consider these equations one at a time. In the first equation, one mole of copper is etched at the expense of one mole each of hydrogen peroxide and sulfuric acid. Therefore, one must add these two chemicals as more copper is introduced to the system. This can best be done by metering pumps. For each pound of copper etched, 0.185 gallons of 50% hydrogen peroxide and 0.10 gallons of concentrated sulfuric acid are consumed. By estimating the loading of copper, the pumps can be set accordingly.

Equation two illustrates the tendency for hydrogen peroxide to decompose, particularly at high temperatures. In the pioneering days of etching in this manner, equipment damage was intolerably high. Today, however, stabilizers are metered in a long with peroxide and acid to minimize this behavior. A more convenient alternative is to use a proprietary blend of peroxide and stabilizer, although it costs a bit more than if purchased separately. The additive is actually composed of proprietary rate exhaultants, solder inhibitors, banking agents, and stabilizers which are developed and sold by various vendors. It is the brand of additive, or "replenisher", that characterizes the particular etchant, (just as a plating bath is characterized by the brand of brightener used). When purchased separately, replenisher is added by simply setting it´s metering pump to one-third the rate for peroxide. There is a somewhat tedious method for analysis, but it is generally only necessary when symptoms such as solder darkening or a higher-than usual peroxide depletion is detected. Normal depletion through decomposition is most prominent in the morning after a period of idleness, and usually requires that a gallon or two of peroxide be added to the sump prior to start up.

The final product of the etching process, copper sulfate pentahydrate, is shown in equation three. In order to etch consistently, it is necessary to remove copper from the system. Failure to do so will result in a slowing down of the etch rate, a more rapid depletion of the peroxide and, ultimately, a re-deposition of copper on to the panel. In the latter case, copper sulfate crystals actually form on the board, acting as a barrier and preventing further etching directly beneath. The result is a panel with unwanted copper appearing as feather-like "crystals".

Most large scale peroxide-sulfuric etching systems rely on a chiller and screw conveyor to remove copper in a continuous mode. A small pump is used to transfer heated working solution from the etcher sump an into a conical bottom tank, which is lined with cooling coils. The chiller maintains the tank at 70° F, which lowers the solubility of copper sulfate in solution, thus causing a solid precipitate to "rain" down and in to the screw conveyor at the bottom. The conveyor brings the crystals up a tube, eventually de-watering them as they emerge above the solution level and droping them into a shipping drum. The crystals can be sold to agricultural or fertilizer refineries, where they can be further processed and copper reclaimed for beneficial reuse. (The zinc backing on copper clad laminate makes its way into the crystals, making them undesirable for metal finishing shops.)

Anyone considering the utilization of this etchant chemistry should investigate their options regarding the ultimate fate of the crystals. Many recycling activites are now falling under RCRA regulations. Multiwire crystals are currently being recycled by a chemical manufacturer that is a permitted hazardous waste treatment/storage/disposal facility. Approximately 10,000 pounds of crystals are shipped from Multiwire each month.

The solution make-up is composed of the following:

84% v/v proprietary make-up solutiion.
12% v/v hydrogen peroxide (50%)
4% v/v proprietary replenisher (stabilizer)

The make-up solution contains the sulfuric acid necessary and eliminates the risky and time-consuming task of adding such a quantity (50 gallons or more) to achieve a 20% vol./vol. concentration. Multiwire's 590 gallon system (crystalizer tank included) consists of nearly 120 gallons of pure acid. Adding this quantity at once would take several hours in order to minimizie the heat generated.

After the make-up is distributed between the etcher sump and crystalizer, the peroxide and replenisher are added. The solution is then ready to be brought up to the 130°F operating temperature.

During the first few days of start up, control of the solution will require fine tuning. It takes a day or two for the recovery unit to begin generating crystals and during this time, the chemical and fluid dynamics of the entire system approach an equilibrium. The crystal-growing convection currents inside the crystalizer, the build-up of copper in the system, and the flow of solution into the recovery unit and back, all interact and gradually work together. After adjusting the metering pumps, the fluid transfer rate, and the agitation inside the crystalizer over the course of a few days, the operation takes on a smooth and orderly fashion. Keep in mind that the best way to fine tune the system is to push the etcher to its limits: load it up with work and get as much copper into the system as would in a full production mode.

The etch rate of peroxide sulfuric is approximately 90 seconds for one-ounce copper - a snails pace, compared to ammoniacal etchants. This can be offset by sizing the machine to meet throughput demands, however.

Process Control

There are three components in the etching solution which effect the etch rate and therefore must be checked periodically. The most critical, of course, is hydrogen peroxide, where a 10-12% concentration is considered ideal for maximum efficiency. Figure 3 illustrates the effect that peroxide has on etch rates.

When Multiwire began etching with peroxide-sulfuric, peroxide additions were totally manual. Proper control required an analysis every 20 minutes, followed by the appropriate addition, usually 2 - 3 gallons. By incorporating a metering pump, only a morning addition is done manually, and an analysis is performed every four hours. The table below illustrates the nominal degree of undercut the Multiwire facility, which is a reflection of good peroxide control (±2%). It should be noted, however, that improper conveyor speeds can increase these lossed by 50% or more, and thus it is important to have qualified operators who are familiar with the etchant.

COPPER THICKNESS	AVERAGE LOSS IN CONDUCTOR WIDTH
3 OZ.	0.0036 IN.
2 OZ.	0.0024 IN.
1 OZ.	0.0012 IN.
1/2 OZ	0.0006 IN.

Dissolved copper also effects the etch rate, but to a lesser degree. The concentration is checked along with sulfuric acid every few hours. Copper content should be kept at a minimum, and this is achieved by either adjusting the rate of transfer to the crystalizer tank, lowering it's temperature, or increasing it's acid concentration. When copper in the etcher sump exceeds 7 oz./gal., the etcher should be shut down for an hour or two and the solution be allowed to circulate through the recovery unit until the concentration drops to 3 - 5 oz./gal.

Sulfuric acid should be of the purest quality (typically electronic grade) and only added to the crystalizer tank. The reason is twofold: the heat given off is more redily extracted in the cold, large volume tank, and high acid content in the etcher will caus crystalization to take place fouling spray mozzles and inhibiting thorough etching.

Etching Characteristics

Peroxide-sulfuric, like all etchants, has a mixed bag of performance characteristics that are worth considering. Etch factors are typically around 1 - 2, somewhat less for print and etch but higher for pattern and panel plated boards (fig. 4). Uniformity is somewhat limited due to puddling, but it is only apparent on large panels where drainage of reacted etchant is slow. It is not uncommeon to pass these under-etched panels through a second time. To minimize this problem, a higher spray pressure is used on the top in order to penetrate the puddling. Vertical etchers are another alternative, which eliminates puddling all together, ensuring even etching on both sides of the panel.

Based on experience, peroxide sulfuric is less forgiving to inadequate photoresist adhesion. Although the etchant is compatable, it tends to soften the resist, possibly due to it's relatively high operating temperature. Haloing and rounded conductor edges can result if good surface preparation practices are not maintained. Most metalic resists are unaffected by the aggressive nature of the etchant, except for nickel-gold, which can result in an excessive undercut of the nickel. This can be avoided by using a sulfur-free nickel deposit, however.

Etching Costs

Based on chemical costs, proxide-sulfuric is somewhat more expensive than alkaline etching. A detailed comparison is beyond the scope of this paper, but the data below will outline the present cost at Multiwire.

CHEMICAL COST TO ETCH 1 LB. OF COPPER

0.169 gal. of hydrogen peroxide @ \$3.40/gal. = \$0.54

0.10 gal. of sulfuric acid @ \$0.50/gal. = \$0.05

0.06 gal of proprietary stabilizer @ \$20.17/gal. = \$1.20

TOTAL ETCHANT COST = \$1.79 per pound cu

An overall cost savings can be realized when including the waste treatment savings. Keep in mind that peroxide sulfuric etchants can be used for an indefinite length of time. The copper waste is a valuable by-product that can be sold or, at worst, given away. Buyers will, in most cases, pick the crystals up on site and thereby free the PC manufacturer of any shipping or disposal charges.

Rinsewater treatment, of course, must always be considered carefully. Probably, the most important benefit of peroxide-sulfuric is the fact that the disolved metal - the most troublesome constituent - exists in a nonchelated state. This makes extraction easy, particularly with precipitation methods. By simply neutralizing the rinsewater with lime, the copper will precipitate as copper hydroxide. Tests have shown that wastewater containing 12 mg/l copper can, by adjusting to a pH of 8, drop the concentration to 0.20 mg/l. There are no sulfides to contend with, and the process is relatively easy to control. The sludge must be dealt with accordingly, however.

The ion exchange method used by Multiwire is distinctively different in that, instead of generating a sludge, a concentrated solution of copper sulfate is the end product. Much like the copper sulfate pentahydrate crystals, this too is a valuable by-product.

Equipment

There are some very important equipment modifications which must be made in order to use peroxide sulfuric in a safe and effective manner. Hydrogen peroxide is a highly reactive material that can seriously damage a machine if the wrong materials of construction are used.

Basically, a conveyorized peroxide-sulfuric etcher is an ammoniacal etcher usually with titanium parts replaced by stainless steel. This includes pump impellors, spray nozzles, and drive chains. Actually, the antimony impurity commonly found in titanium is what makes this metal incompatible. One would regretably discover quickly whether or not a titatium part was accidentally installed, as the violent corrosive action could trigger a runaway exothermic reaction, boiling away the peroxide and warping or even melting the PVC bulkheads of the etcher.

Such a scenario has, undoubtably, haunted the minds of all who contemplate the use of peroxide-sulfuric etchants, and their reluctance is not without good reason. Accidents of this nature, which can be caused by a variety of contaminants, have occurred in the past. However, with the advent of better stabilizers, these exothermic reactions are now rare. The possibility still exists, however, and it is important to protect the etcher from this threat.

To do this, one should use a good amount of stainless steel cooling coils to remove the heat generated. A temperature alarm should be implemented to automatically cool the sump down from above say, 135°F, which is well above normal operating temperature. When the unit is shut down, this same temperature control should cool the solution to 100°F or less in order to minimize a reaction should it occur during idle periods. This will also minimize peroxide consumption due to its instability at elevated temperatures. Cooling solenoids should be of the normally open type, so that in the event of a power failure, water will automatically flood the cooling coils. A pressure switch should be wired to an audible alarm to call attention to any low water pressure situation. Finally, the entire safety system should be on a separate circuit backed by an emergency power source.

This somewhat redundant safety system may sound extravagant, but one cannot be overly prudent. At a cost of a few hundred dollars in hardware, the system will virtually guarantee that the etcher will escape a runaway reaction unscathed. Manufacturers of peroxide-sulfuric etchers will usually have some kind of safety system. When purchasing a new processor, look over these features carefully, and make sure they cover all "what if" situations.

The ideal peroxide-sulfuric etcher would be made of stainless steel, which would enable it to survive the high temperature easily, save for any plastic roller wheels or expendable o-rings. But steel is expensive, and that is why most etchers remain PVC or polypropylene. Polypropylene is able to stand higher temperatures that PVC, but welds made of this plastic have been known to get attacked by peroxide unless fabricated with hot nitrogen has rather than air.

Aside from the extra cooling and the materials of construction, the only other departures from traditional etcher design is the copper recovery unit. Although most users of conveyorized peroxide-sulfuric use an automatic system, it is not a mandatory accessory. Simply by decanting the liquid etchant from a drum where it has been allowed to cool, the copper sulfate is effectively removed. A continuous recovery system is, however, far more practical. There is no labor, no machine downtime, and it maintains a constant copper concentration. With a heat-exchanger included, a system can cost as much as the etcher itself. In order to fully appreciate the benefits of peroxide-sulfuric etching, however, it is a worthwhile investment.

A properly designed crystalizer should consist of a sturdy, conical bottom tank with a mixer placed directly in the center. The shaft of the mixer should be surrounded by a steel "draft tube". The tank is lined with cooling coils through which water or a 20% glycol ether solution flows. A chiller, sized accordingly and either air or water cooled, maintains the coolant at 60°- 70°F.

If the local water supply remains cool enough throughout the year, a chiller may not be necessary. A chiller is preferred, however, because it allows for better process control while it also expands the heat exchanging capacity. A considerable savings in water usage is another benefit.

The crystalizer tank should be designed such that as hot etchant is pumped into the draft tube, the mixer pulls the solution down then out and up the side of the tank as in fig. #5. As crystals form they circulate in this fashion while growing in size. Finally, their weight frees them from the convection and they fall into the auger. The crystals are never actually "dry", but more like wet sand. The liquid tends to build up as the crystals fill the drum, and it may be necessary to drain some of it off before it can be transported. The cohesive attraction of the liquid to the crystal surface seems to make this problem somewhat formidable.

Other recommended features include a temperature monitor, a high temperature alarm, and a variable speed control for the mixer motor. Appropriate fittings should be provided for a fresh water hook-up should the chiller ever malfunction. There have been cases where a chiller is down for over a week before a replacement part arrives. By simply connecting a garden hose to the cooling coil, production disasters are avoided. Multiwire took this concept a step further and, through a series of solenoids valves and a temperature sensor, automated the system for back-up cooling control.

Summary

As governments impose tighter restrictions on industrial effluents, the cost of waste treatment becomes more of a burden to manufacturers. Any process method that can lighten the load, from a treatment standpoint, should attract the attention of cost-conscious manufacturers. Peroxide-sulfuric etchants fall into this category of easy-to-dispose chemical systems, but to call it cost effective would be pre-mature. At Multiwire, peroxide-sulfuric etching fits in well with the rest of the process, but it may not be compatible in every P.C. shop. One should consider carefully the operational, waste treatment and conversion costs before deciding whether or not it is cost-effective. Finally, in order for the etchant to perform well, it is important to have well designed equipment for applying it, and reliable personnel to fully understand it.

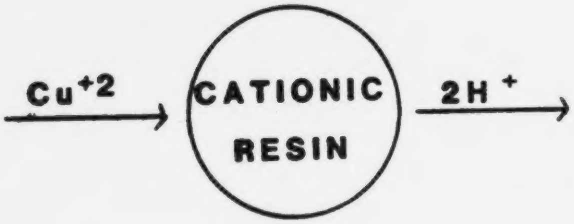

Cu+2
CATIONIC RESIN
2H +

Fig. 1

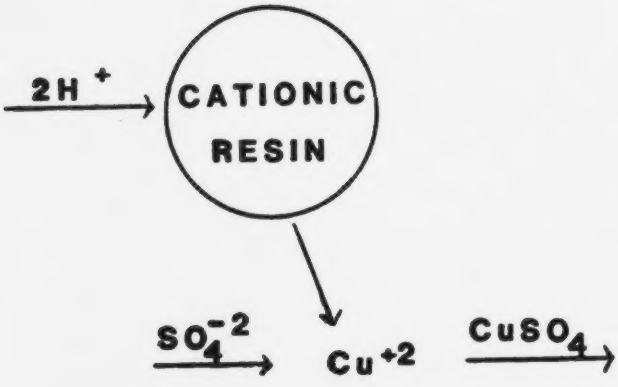

2H +
CATIONIC RESIN
SO4-2
Cu+2
CuSO4

Fig. 2

E12

HYDROGEN PEROXIDE CONCENTRATION vs. ETCH RATE

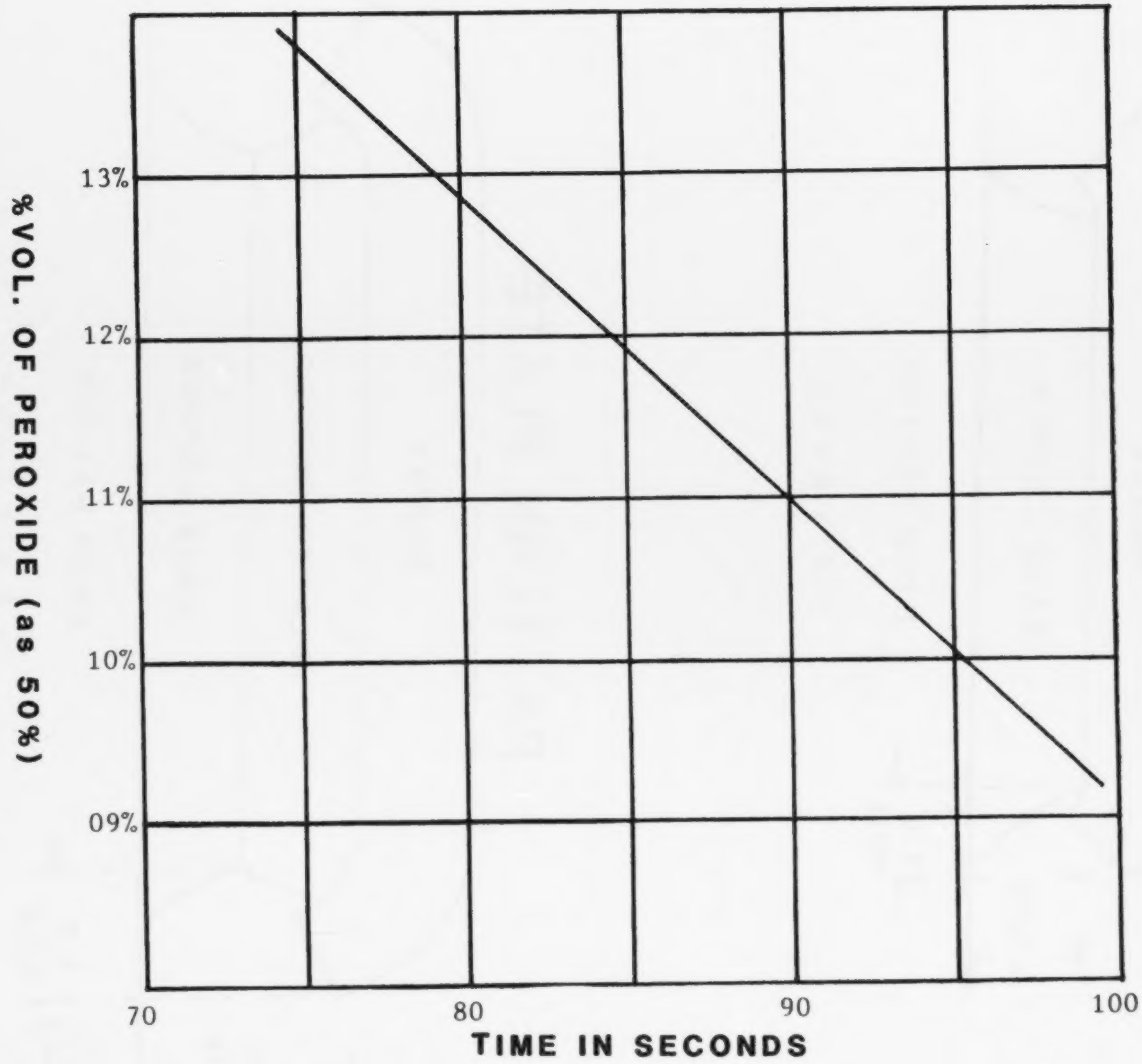
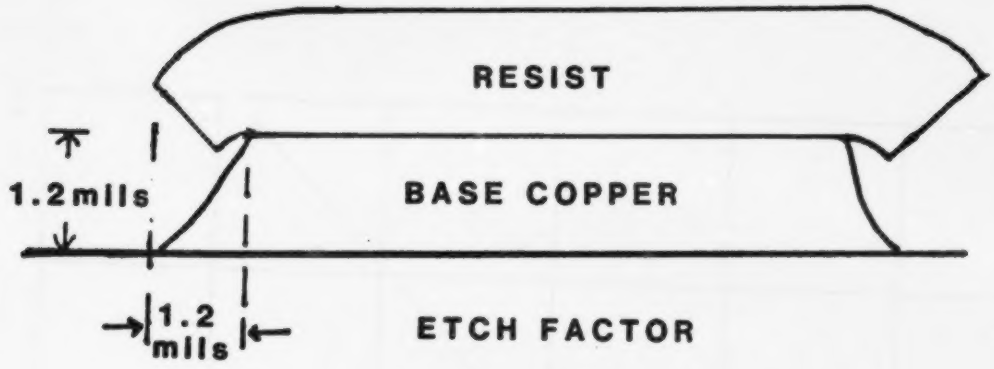


Fig.3

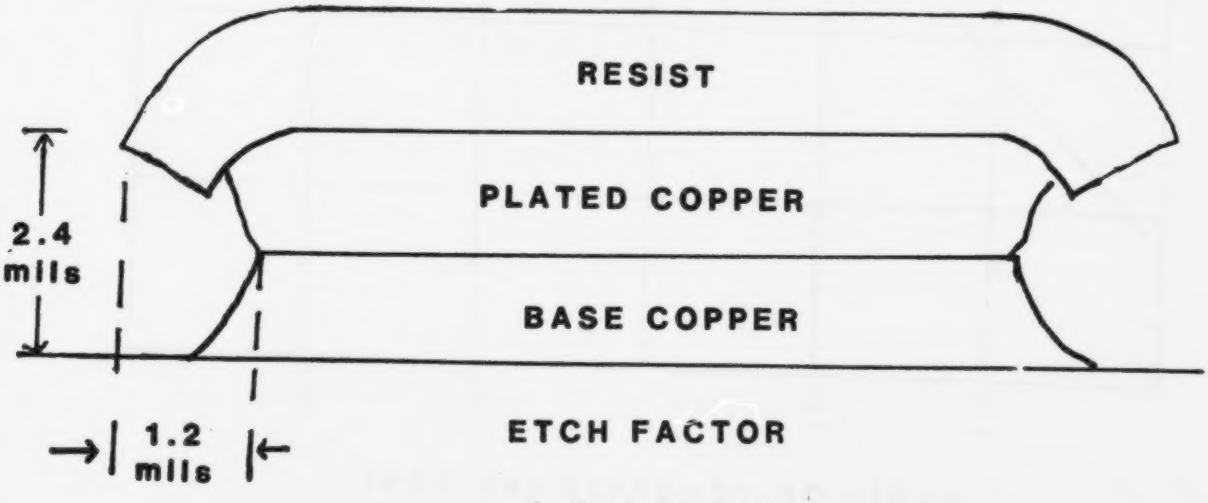
PRINT&ETCH


RESIST
1.2mils
BASE COPPER
1.2 mils

ETCH FACTOR

1.2/1.2=1.0

PATTERN PLATE


RESIST
2.4 mils
PLATED COPPER
BASE COPPER
1.2 mils

ETCH FACTOR

2.4/1.2=2.0

Fig.4

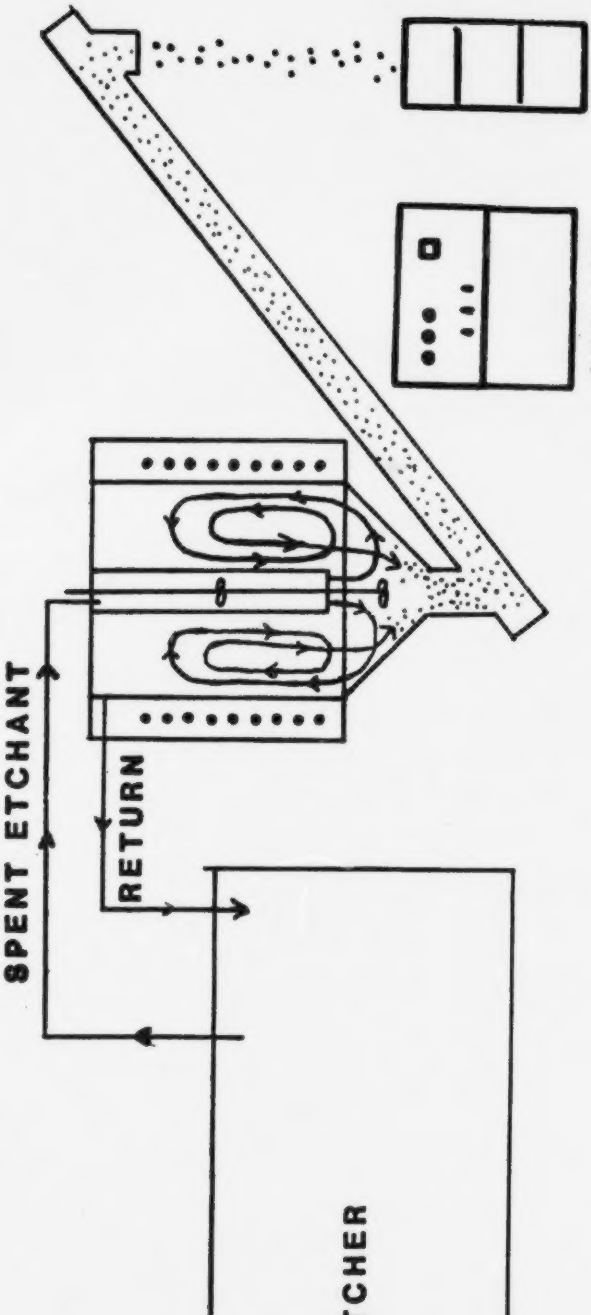

SPENT ETCHANT
RETURN
CHILLER
ETCHER

Fig.5

REVERSE OSMOSIS FOR INDUSTRIAL WASTE TREATMENT

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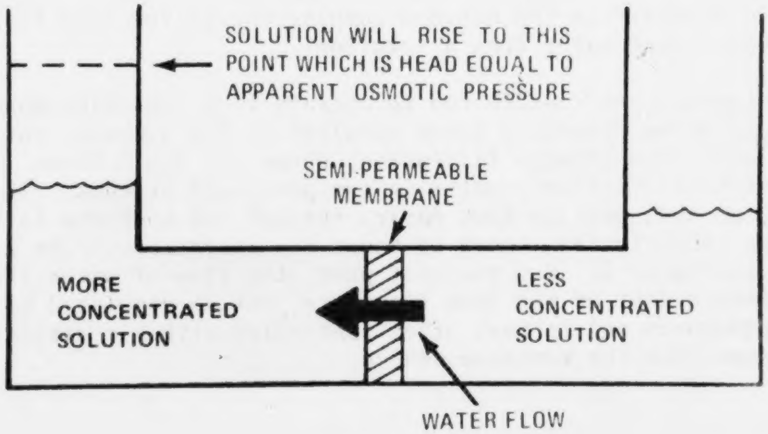
Introduction

The treatment and disposal of heavy metal wastes have always been of concern to plating operators. New environmental legislation is making dispoal of the effluent generated from some chemical precipitation treatment systems difficult. Therefore, operators are looking for solutions to this disposal problem. Reverse osmosis (RO) has been examined and found to be effective in treating this clarified effluent for reuse in plant processes and/or direct disposal.

Technical

RO is a low energy separation process utilizing a semipermeable membrane. When a semipermeable membrane, such as a cell wall, separates two solutions of different concentrations of dissolved solids, pure water will flow into the concentrated solution. This movement of water is due to the difference in potential energy across the membrane and is known as osmosis. The semipermeable membrane restricts the movement of ions but allows pure water to pass until an equilibrium energy state is achieved. The process of osmosis is depicted in Figure 1.

Figure 1


SOLUTION WILL RISE TO THIS POINT WHICH IS HEAD EQUAL TO APPARENT OSMOTIC PRESSURE
SEMI-PERMEABLE MEMBRANE
MORE CONCENTRATED SOLUTION
LESS CONCENTRATED SOLUTION
WATER FLOW

F1

OSMOSIS

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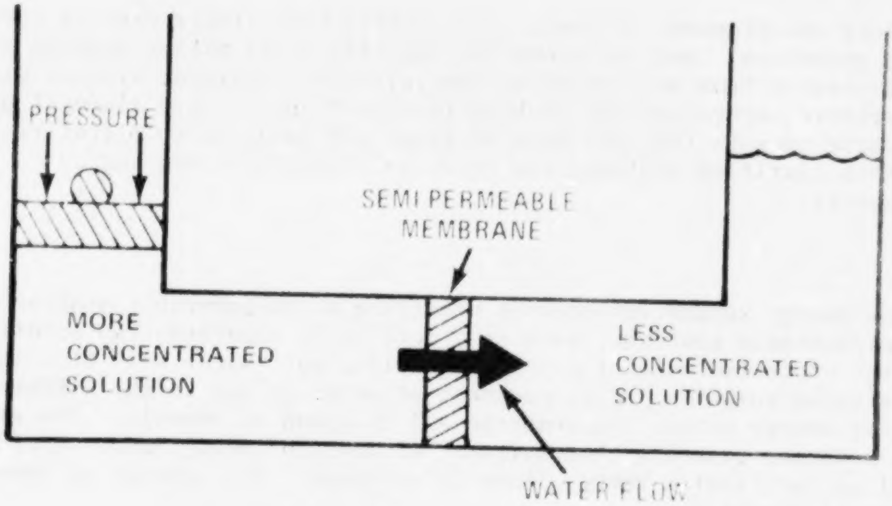
By applying pressure to the more concentrated solution the normal osmotic flow is reversed and pure water is forced through the semipermeable membrane into the less concentrated solution. In the process of RO, this applied pressure is usually provided by a pump and amounts to adding energy to the more concentrated (lower-energy) side of the membrane. RO is depicted in Figure 2.

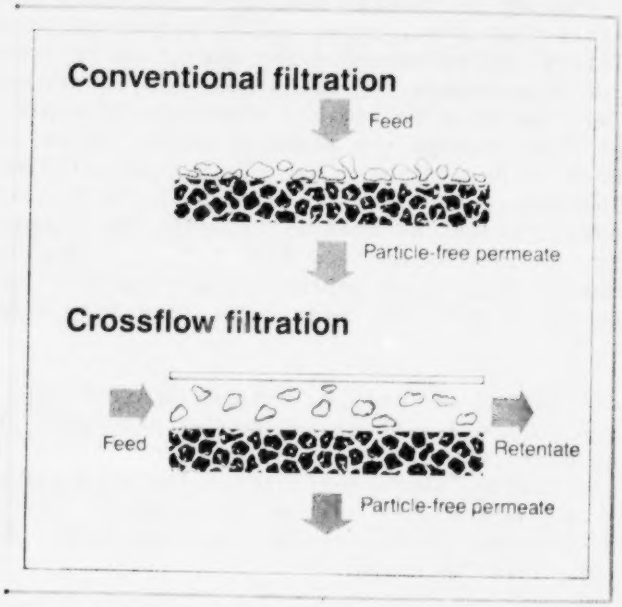


REVERSE OSMOSIS

The force exerted by the concentrated solution is known as osmotic pressure and is proportional to the concentration of dissolved solids. In practical terms, osmotic pressure is the minimum pumping energy required to produce the first drop of pure water from a solution.

RO membrane elements are constructed to operate in a crossflow manner. This means the fluid being processed flows parallel to the membrane surface. Unlike conventional flow-through filtration, where all fluid flows through the filter, crossflow filtration results in two processed streams. The purified portion, or that portion that passes through the membrane is known as permeate. The concentrated stream is known as concentrate. The processes are depicted in Figure 3. For the most part, the flow of water through the membrane is independent of the feed flow rate, but is regulated by the transmembrane pressure and is most often controlled with a restricting valve downstream from the membrane device.

Figure 3



The production rate of an RO membrane element is a function of such variables as membrane type, concentration of dissolved solids, temperature of the feed solution and applied pressure. Since the composition of each waste stream is different, it is impossible to predict performance without pilot testing. Typically, initial testing is performed on a 50 gallon representative waste water sample. Such testing is the most economical means of determining the feasibility of the process. Testing also determines if the membrane polymer is chemically compatible with the solution being treated.

It is important during testing to optimize system recovery. Recovery is the ratio between permeate and feed flows, and is usually expressed as percent. With waste water applications, it is usually desired to operate at recoveries as high as possible. As recovery is increased, the concentrate stream will increase. This increase can be rather marked; for example, the concentration of salts in a system operating at 98% recovery is 2.5 times greater than that of a system operating at 95% recovery. As the concentration increases it becomes necessary to operate at higher feed pressures to overcome osmotic pressure effects. System design must take into account materials that can tolerate the pressures encountered. Also, since membranes always pass a small percentage of the total dissolved solids present on the feed side of the membrane, permeate quality is lower in high recovery systems. Therefore, permeate quality must also be checked to see that process requirements are met. Generally, enough data are generated during a batch pilot test to produce a preliminary system design and estimate process economics.

An important design characteristic that can not be determined during a batch test is membrane fouling. Fouling is the number one factor affecting RO system performance. Fouling is usually caused by suspended materials in the feed stream or materials that precipitate during processing. Generally, at least 5 micron prefilters are recommended for operation to remove suspended materials. The use of dispersants, pH adjustment of feedstream or changing system recovery are all employed to inhibit materials from precipitating. Maintaining turbulent flow through the membrane device minimizes fouling by preventing suspended or precipitated materials from settling on the membrane surface. Turbulence is often promoted with the use of special membrane spacers and configurations as well as changing the pumping rate. Reducing system recovery by increasing feed flow rate or reducing permeate production rate (membrane flux) also improves performance. Improved performance results from the higher crossflow velocities and increased turbulence.

Since fouling characteristics can only be determined from long term testing, batch testing is often followed with an onsite "slip-stream" evaluation. This phase of testing must take into account any fluctuations in the process and determine membrane fouling characteristics. The slip stream approach is an inexpensive means of guaranteeing system performance. Process changes are readily made and membrane fouling can be characterized. Membrane cleaning procedures are also developed.

Case Histories

1) Printed Circuit Board Waste

A west coast printed circuit board manufacturer has constructed a new building to accommodate an expanding operation. Most of the waste is generated during subtractive etching of copper clad laminate. Nickel, lead and chrome wastes are also generated but in a smaller quantity than copper. The waste streams are treated in a mixed effluent chemical precipitation system. Precipitation is enhanced with a proprietary polymer and solids are removed in a slant tube clarifier. Testing has shown the precipitation system to be very effective in removing toxic metals. The resulting effluent contains about 2000 ppm of total dissolved solids (TDS), mostly sulfate salts and organics (surfactants). No means of discharging this effluent stream exists at the new plant site; therefore, it is desirable to recycle as much water back to the process as possible.

Evaporation, electrodialysis and RO were considered for salts removal. Since economics favor RO, pilot testing was performed to determine process feasibility. A representative 55 gallon waste sample was collected and filtered through activated carbon for organics removal. Membranes from several manufacturers were evaluated for chemical compatibility and performance before and after testing with a standard salt solution. A spiral wound thin film composite type membrane was selected as the best choice because of its high rejection. Test data are presented in Table 1.

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Table 1

	Unfiltered feed solution	Permeate at 95% recovery	Concentrate at 95% recovery
TDS, ppm	2110	158	22500
pH	12	-	--
Lead, ppm	<0.1	<0.1	--
Copper, ppm	0.15	<0.05	--

< means "not detected at this level"

System operating data are presented in Table 2

Table 2

Time (min)	Pressure (psi)	Permeate flow (gpm)	Concentrate flow (gpm)	Permeate concentrate (ppm)
5	620	1.8	0.08	90
10	640	1.7	0.08	130
15	630	1.6	0.08	150
20	630	1.6	0.08	160
25	650	1.6	0.08	170
30	640	1.5	0.08	160

It was necessary to halt testing after 30 minutes because increasing temperatures made accurate data collection impossible. Note the slight decrease in flux rates over the time of this test. This change in flux is probably due to either fouling of the membrane with suspended or precipitated materials or constituents of the waste stream chemically affecting the membrane.

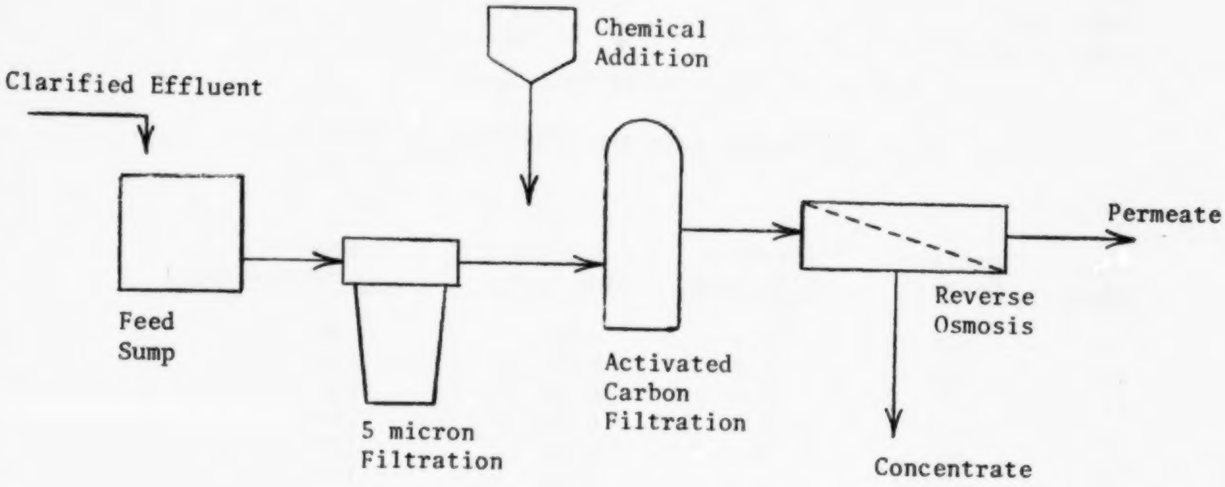
Membrane flux and rejection were measured with a standard 0.2% NaCl solution before and after testing on the waste stream. These data are presented in Table 3.

Table 3

Time	Pressure (psi)	Permeate flow (gpm)	Concentrate flow (gpm)	Permeate concentrate (ppm)
Before	400	1.4	2.0	28
After	400	1.4	2.0	31

Note that baseline data are nearly identical before and after testing. Therefore, the membrane is chemically compatible with the solution being processed.

Since data appeared favorable, an onsite pilot plant study on a waste water slip-stream was performed to determine long term performance. The pilot test was performed at as near actual operating conditions as possible. A pilot run schematic is presented in Figure 4.


Chemical Addition
Clarified Effluent
Permeate
Feed Sump
5 micron Filtration
Activated Carbon Filtration
Reverse Osmosis
Concentrate

On start up of pilot equipment a rapid flux decrease was observed. These data appear in Table 4. A sample of RO concentrate was collected and a fine white precipitate was observed. A check of waste treatment operation revealed that operators periodically added lime ($Ca(OH)_2$) to improve performance. Unfortunately, the system had been dosed with lime just prior to start up of the pilot run. Therefore, the precipitate was assumed to be calcium sulfate ($CaSO_4$). The use of a chemical dispersant did little to improve RO system performance. The precipitated material was readily removed from the membrane with an acidic membrane cleaning solution. However, membrane fouling was too rapid and severe to justify specifying a system. Therefore, it was necessary to perform process changes.

Table 4

Time (min)	Temp. (F)	Feed Press. (psi)	Perm. Flow (gpm)	Conc. Flow (gpm)	Recycle Flow (gpm)	Feed Conc. (ppm)	Perm. Conc. (ppm)
15	72	700	1.25	0.05	7.5	--	--
30	72	720	1.10	0.05	8.0	1900	50
45	70	630	0.55	0.05	8.0	1900	65
60	70	660	0.35	0.05	8.5	1900	100
75	71	670	0.24	0.05	8.5	1900	65
90	71	680	0.21	0.05	8.5	1900	65
105	70	680	0.17	0.05	8.5	1900	65

All lime was replaced with caustic soda (NaOH) and allowed to flush itself from the waste treatment system. RO performance was reevaluated. No membrane flux loss was observed but prefilters were rapidly fouled since floc formation was poor. Therefore, a different polymer floccing agent was selected for its improved performance. Also, membrane flux rate was reduced to about 12 gallons per square foot day (GFD) at start up by reducing the feed pressure. The feed flow rate was adjusted to maintain a 10% minimum recovery per membrane pass.

These steps proved successful in maintaining pilot run performance at acceptable conditions. Performance was maintained for several weeks and all bath dumps and rinses were evaluated with no negative effects.

The process was determined to be feasible and the data generated during this pilot run were used to specify a two pass system design. The first pass operates at 75% recovery and increases solution concentration about four times. This concentrated solution is then processed with a second RO system operating at 80% recovery. The resulting concentrate is about 50,000 ppm TDS,which will be hauled away. The two pass design is necessary to maintain average membrane fluxes at acceptable levels. Overall recovery is 95%. Future testing will be performed to evaluate the economics of evaporating the final concentrate solution to dryness.

The RO portion of this waste treatment system is now being installed. Start up is scheduled for late February, 1986. This system will operate as three separate units, holding one on a stand-by basis for continuous operation. At full production the system will process 40 gpm.

II) Wire Coating Waste

A west coast wire coater has discharged his rinse waters and spent baths to evaporation ponds. Recently, the State has forced closure of these ponds. Therefore, it became necessary to install a waste treatment system. Chemical testing was performed to optimize precipitation chemistry and specify equipment. Since no sewer exists it is necessary to recycle rinse waters back to the process. Total dissolved solids must be less than 2000 ppm to meet process requirements. The supernatant resulting from the precipitation system contains about 20,000 ppm TDS; therefore, further processing is required.

Again, economics favor RO. Unfortunately, time did not allow for extensive pilot testing, so an onsite batch pilot evaluation was performed. 50 gallon representative samples were collected and batch treated chemically for metals removal. The resulting supernatant was filtered with activated carbon and passed through five micron prefilters prior to RO processing. Several RO membranes were evaluated and a spiral wound thin film composite type membrane was again selected as the best choice. Testing showed improved membrane performance resulted when an excess of sodium bisulfite was added to the solution. RO performance was monitored and data are present in Table 5.

Table 5

Time (min)	Permeate Flow (gpm)	Recycle Flow (gpm)	Concentrate Flow (gpm)	Feed Pressure (psi)	Temp (F)	Permeate Conc. (ppm)	Recovery (%)
0	0.5	8.0	0.2	340	64	630	73
30	0.55	8.0	0.2	340	66	630	73
60	0.55	8.0	0.2	340	70	640	73
90	0.55	8.0	0.2	600	74	640	73
120	0.55	8.0	0.2	600	74	630	73
150	0.55	8.0	0.2	600	72	650	73
180	0.55	8.0	0.2	600	74	650	73
0	0.5	8.0	0.1	620	72	780	83
30	0.5	8.0	0.1	620	72	820	83
60	0.5	8.0	0.1	620	72	820	83

Note that RO performance was good. Unfortunately, time did not allow for a more extensive long term pilot evaluation. Based on data generated a "worse case" design was prepared. Membrane flux is to be maintained at low levels, about 12 GFD, to minimize fouling. To provide a variable feed pressure to the membranes, a piston pump was specified. The system was designed to process 7.5 gpm of effluent at 85% recovery and utilizes 12 membranes - three banks in parallel of four membranes each. Initially, the concentrate will be hauled off-site for disposal. A minimum pump flow of 20 gpm is required to maintain turbulence in the system.

This system is now in the construction stage and start up is scheduled for February. Since little is known of long term performance, optimization will be finalized during actual system performance.

Conclusion

This paper has shown RO to be effective in processing end-of-pipe industrial waste for recycle and discharge. As new legislation is imposed, RO will continue to be a viable alternative to meet new discharge requirements. New developments in membrane polymers and innovative process design will lead to further acceptance of this low energy technology in the future.

COPPER, NICKEL, AND CHROME RECOVERY IN A JOBSHOP TO ELIMINATE WASTE TREATMENT AND SLUDGE DISPOSAL

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Pickering, Ontario, Canada

G.G. Buffing and Plating is a job plating shop in Montreal, Quebec that plates decorative copper, nickel, chrome and hard chrome on a variety of automotive and motorcycle components and trim.

In 1984 G.G. Buffing decided to expand it's facilities. Since they were located in a high density urban area, the area available for expansion was limited. It was decided to build a two-story addition to the existing plant that would house a new plating line on the ground level and all services (scrubbers, rectifiers, pollution control) on the upper level. In order to receive permission from the City of Montreal to proceed with the expansion, G.G. Buffing was required to submit details of their planned waste treatment system to demonstrate that they would be in compliance with local effluent discharge standards. Local requirements were 5 ppm for each of copper, nickel, and chrome.

Conventional precipitation and destruction waste treatment was considered. However, while this approach would allow the plant to meet the discharge limits, it was also recognized that operation of a waste treatment system would represent an ongoing cost with no chance of any payback. With the current trend of escalating costs for disposal of metal hydroxide sludges, the operating cost of such a system would only increase in the future. It was decided to use chemical recovery in order to meet the discharge limits while reducing operating costs. After evaluation of a number of recovery technologies, patented (1) short bed ion exchange was selected for a number of reasons.

1. The equipment was compact and could fit into the second floor of the new building.
2. While copper, nickel, and chrome rinses required separate systems, the equipment was similar in design and operation. This would make it easier for the operators to be able to understand and maintain the systems.

3. Visits to other installations confirmed that the technology was proven and the equipment was reliable.

The systems were installed late in 1984 and started up in early 1985. Each of the recovery systems are connected to the plating operation in a similar manner as shown in Figure 1. The copper, nickel and chrome plating baths are each followed by three 600 gallon rinse tanks designed to accommodate counter current flow. The quality of the water in the first rinse is monitored by a conductivity probe. When the dragout of plating solution into the first rinse increases the conductivity above a set-point, deionized water is automatically introduced into the third rinse. As the rinses counterflow forward, the rising level in the first rinse activates a level controller which starts a pump transfering rinse water up to the second floor feed tank for the respective recovery system. The ion exchangers remove the dissolved metal from the rinse water. Treated copper and nickel rinse waters then flow to a final pH adjustment pit and are discharged. Treated chrome rinse water is recycled. Periodically, the ion exchangers automatically regenerate to yield a concentrated metal salt solution which is recycled to the appropriate plating bath.

Copper Recovery Operation(Figure 2)

Copper is plated out of a copper sulfate solution. Rinse water from the first rinse following plating is transferred to a feed tank for the copper recovery unit. The copper recovery unit begins operation when initiated by a level controller in the feed tank. Rinse water at about 38 lpm flows through a carbon column to remove organic brightener additives, then through a cartridge pre-filter to remove suspended solids and, finally, down through a short (15 cm. high, 30 cm. diameter) column of fine-mesh cation exchange resin. Copper cations in solution are exchanged for hydrogen cations on the resin. The copper concentration of the rinse water is reduced from about 300 ppm to less than 1 ppm. Despite the fact that the water leaving the recovery unit is essentially free of copper, the water is not recycled to copper rinsing. This is because the exchange of copper for hydrogen makes the water acidic. Recycling it to the copper rinses would interfere with the operation of the conductivity controller in the first rinse and would eventually reduce the effectiveness of the recovery unit to remove copper.

After a set time, the flow of rinse water through the cation exchanger is automatically stopped. This time is determined based upon the concentration of copper in the first rinse, the flow rate through the recovery unit, and the cation exchanger's capacity to effectively maintain a low concentration of copper in its effluent. With the flow of rinse water stopped, the recovery unit goes through an automatic regeneration sequence. Dilute (about 10%) sulfuric acid regenerant is passed up through the cation exchanger. The initial volume leaving the exchanger is displaced rinse water which is diverted back to the feed tank. As the sulfuric acid passes through the cation exchanger copper is exchanged from the resin for hydrogen. A concentrated copper sulfate solution then leaves the exchanger and is diverted to a holding tank. Water then flows down through the exchanger, rinsing the excess acid and copper solution back into the vessel used to automatically make-up the regenerant solution for the next regeneration. This "reciprocated wash" ensures that sulfuric acid is used efficiently and that no copper is lost during regeneration.

The regeneration sequences takes only about one minute. The recovery unit is then ready to begin another cycle of treating rinse water as required.

The concentrated copper sulfate solution recovered from the rinse water is added to the copper plating bath when needed.

Nickel Recovery(Figure 3)

Both Semi-bright and bright nickel plating is carried out in Watts-type baths. Bright nickel plating rinse water is transferred to the recovery unit feed tank as described above. The nickel recovery unit begins operation when initiated by a level controller in the feed tank. Rinse water flows at about 38 lpm through a cartridge pre-filter to remove suspended solids then down through a short (30 cm. high, 30 cm. diameter) column of fine-mesh cation exchange resin. Nickel cations in solution are exchanged for hydrogen cations on the resin. The nickel concentration of the rinse water is reduced from about 500 ppm to less than 1 ppm. As with the copper recovery system, the water is not recycled to the rinses for the same reasons, plus one more. The rinse water contains organic plating bath additives. These organic additives, being anionic or non-ionic in nature, are not removed by cation exchange. Continued recycling of this water would result in a high organic concentration in the rinse water. This condition can result in an organic film forming on the nickel surface that will affect chromic acid plating resulting typically in 'whitewash' at high current density areas.

After a pre-set time, as with the copper recovery unit, the flow through the cation exchanger stops and an automatic regeneration sequence begins. Regeneration begins in a similar manner as with the copper recovery unit. Dilute (about 10%) sulfuric acid regenerant is passed up through the cation exchanger to exchange hydrogen for nickel. After the displacement of rinse water, a concentrated nickel sulfate solution leaves the cation exchanger.

At this point the nickel sulfate solution has a pH of 0.8 - 0.9 due to the excess sulfuric acid required to effectively regenerate the resin. If such an acidic concentrate were added to the nickel plating bath it would result in an unwanted depression of the operating pH from the desired valve of 4.0. In order to raise the pH of the concentrate, it passes immediately through a second resin column containing a sorption resin which has the unique ability to 'sorp' the excess acid from the nickel sulfate. The concentrate leaves this column with a pH in the acceptable range of 3.0 - 3.5 and flows to a holding tank awaiting recycle to the plating baths. A "reciprocated wash" of the resin columns with water "regenerates" the sorption resin while rinsing the regenerated cation resin and recovering excess acid and nickel sulfate for the subsequent regeneration. Again, nickel loss is prevented and acid consumption is reduced. Once this wash is completed, the unit is ready to being another automatic cycle.

Chromic Acid Recovery (Figure 4)

Chrome is plated out of a chromic acid solution. Plating rinse water is transferred to the recovery unit feed tank as described above. From the feed tank rinse water flows through a cartridge pre-filter to remove suspended solids, then down through a short (15 cm. high, 30 cm. diameter) column of fine-mesh cation exchange resin. Cationic contaminants such as trivalent chrome, iron, nickel and copper are exchanged for hydrogen by the resin. The rinse water then continues on through a short (7 cm. high, 30 cm. diameter) column of fine-mesh anion exchange resin where the various chromate anions are exchanged for hydroxide anions by the resin. Deionized water leaves the anion exchanger and is recycled to the final chrome rinse and counter flows forward. The quality of the water leaving the recovery unit is continuously monitored by an in-line conductivity controller. When the conductivity exceeds 90 micromhos, the flow of water leaving the recovery unit is diverted from the final rinse to the first rinse. By recirculating the first rinse tank, the anion exchange resin is more fully loaded with chromate without impairing the rinse water quality. After fifteen minutes, the flow of rinse water stops and an automatic regeneration sequence begins.

During regeneration a dilute (10%) sulfuric acid solution regenerates the cation exchanger. The regenerant flows to final pH adjustment and is discharged. Metallic contaminants present in this waste are sufficiently low that the final plant effluent does not exceed the discharge limit. Meanwhile, dilute (5%) caustic soda regenerant flows up through the anion exchanger, exchanging chromate for hydroxide. The sodium chromate solution leaving the anion exchanger then flows through another cation exchanger which exchanges sodium for hydrogen, thereby producing chromic acid. The chromic acid flows to a storage tank. Water rinses the excess chromate and caustic out of the exchanger columns back into a reservoir for the subsequent regeneration. In this way chrome loss and regenerant chemical consumption is reduced.

The chromic acid produced by the recovery unit has a higher chromate:sulfate ratio (50:1) than the plating bath (150:1) due to the pick-up of some sulfuric acid from the cation exchange resins. This is easily corrected by the addition of a small amount (typically 0.7 kg./day) of barium carbonate to precipitate the excess sulfate. The chemical treatment is performed automatically in a small tank that provides mixing, settling and transfer of the treated chromic acid to a final holding tank prior to recycle to the plating bath.

Operating Experience

The recovery equipment arrived at the plant as pre-assembled, skid-mounted, automatic units. Installation was carried out by G.G. Buffing personnel following written instructions provided by the equipment supplier. This consisted primarily of running inter-connecting PVC piping. The systems were started up by the equipment supplier and G.G. Buffing personnel were trained in its operation. Noteworthy experiences of the first ten months of the systems' operation are summarized below.

1. Shortly after startup,

   The chromic acid recovery system encountered a problem of "fouling" of the anion exchange resin by metallic hydroxide precipitates. This was traced to suspended solids passing from the chrome rinses into the recovery unit's cation exchanger. This prevented effective removal of cationic impurities (trivalent chrome, nickel, copper) which then passed to the anion resin (in the hydroxide form) and precipitated. The situation was corrected by physically cleaning the chrome rinse tanks which had contained an accumulation of solids since startup. Also, the recovery unit's pre-filter cartridges were changed from nominal 10 micron to a nominal 1 micron. The ion exchange resin was cleaned and the unit was restarted.

2. After approximately ten months of operation, the nickel plating bath experienced some problems with anode bags becoming clogged due to calcium sulfate crystallization. It was determined that although deionized water was being supplied to the nickel rinses, the recovery unit was using 240 ppm T.D.S. city during its "reciprocated wash" after regeneration. Calcium was entering the system at this point, exchanging on to the resin, then being regenerated off and transferred to the plating bath along with recovered nickel. This situation was corrected by replacing the unit's water supply with D.I. water.

3. One concern with nickel recovery in duplex (semi-bright/bright) nickel plating operations is cross-contamination of organic additives. In particular, the sulfo-organic additives of a bright nickel plating bath can adversely affect the corrosion resistance of the nickel deposit if they are introduced into the semi-bright bath. This fact is important because it is the bright nickel bath that is dragged into the rinses, yet it is the semi-bright bath that is depleted of nickel and requires the nickel addition. Since the organic additives are anionic or non-ionic, they are not exchanged on to the cation exchange resin along with the nickel. In order to confirm this, a test was conducted in which nickel was plated out of a solution prepared with recovered nickel sulfate. The nickel plate was then analyzed for sulfur content. The results showed there to be less than 0.002% sulfur in the plate. In this standard test a level of less than 0.006% is considered acceptable for semi-bright nickel deposits. On this basis the recovered product was deemed suitable for recycle to either of the nickel plating baths.

4. On occasion, the units would pass through a phase of poor operation for a day or two. At first this appeared to be a "bogey man" problem, but the cause was later found to be air locks in the piping from the regenerant acid and caustic storage tanks. These air locks could occur if the storage tank was allowed to drain completely prior to refilling. Daily monitoring of the tank levels to ensure that they did not run dry have successfully kept the "bogey man" at bay.

5. Monitoring and maintenance of all of the recovery units was carried out by the Plating Manager, Tom Nadeau. This has required an average of one and one half hours per day. Monitoring consists of completing log sheets noting the individual recovery unit parameters such as flows, pressures, and visual appearance of the rinses. Maintaining such a log was useful when any troubleshooting was required as it provided a convenient history to indicate any trends that may have been developing.

6. It was observed that the throwing power of the chrome plating bath has remained exceptionally good to-date compared with experience prior to using such a recovery system. The previous practice was to return as much of the dragout collected in the first rinse to the bath as evaporation would allow. The improved plating performance was attributed to the elimination of cationic contaminants (trivalent chrome, nickel, iron) being returned to the plating bath due to the nature of the ion exchange recovery process. The result has been a more pure plating bath with lower electrical resistance and so good throwing power.

Performance

G.G. Buffing had specified the recovery capacities of the equipment for chromic acid, nickel sulfate and copper sulfate to be 0.6, 2.5 and 2.3 kg/hr. respectively. After startup, the systems demonstrated recovery capacities of 0.74, 2.8, and 3.28 kg/hr. respectively.

The performance of each of the recovery systems is summarized in Table 1. Note the first rinse concentrations of chrome, nickel, and copper of 170, 460, and 260 mg/L. These represent the concentration of the feeds to the recovery units. The concentration of the recovered products indicates factors of concentration for chrome, nickel, and copper of 311, 69, 135 times. The effluent concentrations are the averaged concentrations over a complete cycle of operation.

It should be noted that these effluent streams only flow when the recovery unit is going through a cycle. If the conductivity controller in the rinse tank detects that the rinse water contamination is below to set point, the recovery unit remains in standby with no flow.

The chrome recovery effluent concentration of 20 mg/L of chrome is typical for this unit. Despite the concentration, the amount of chrome lost is less than 0.7% of the dragout. It is present in the waste stream from the regeneration of the second cation exchanger (used for the conversion of sodium chromate to chromic acid). While the concentration of this point source is high relative to the effluent discharge limit, this waste stream is intermittant and it represents a very small portion of the total plant effluent.

Based upon the 35-45 L/min. effluent flow as indicated in Table 2, the chrome unit effluent would contribute 0.8 mg/L to the final effluent concentration when it is flowing. In making a similar calculation for nickel and copper, the recovery unit effluents are contributing about 0.5 and 0.45 mg/L to the final effluent respectively, yet the analysis of the final effluent consistently showed higher levels of nickel and copper. This was attributed in part to drips during transfer, but it is suspected that most of it comes from spills of small quantities of plating solution while servicing plating bath filters. The small puddles below the catwalk slowly make their way into the waste trench contributing to the nickel and copper levels detected. Collection and segregated treatment of these spills may be required to meet lower limits should they be improved in the future.

Economics

Costs for the recovery of chrome, nickel, and copper by the units have been summarized in tables 3, 4, and 5. Note that in each case a caustic soda consumption is given. Even though no caustic may be used in a recovery unit's operation, it is assumed that this caustic is required for final pH adjustment since the effluent from the cation exchangers will be acidic due to the exchange of metals for hydrogen.

By comparison, the alternative cost of waste treatment and sludge disposal is shown on Tables 6, 7, and 8. The net savings are calculated by difference. The key figure in the waste treatment calculations is the sludge disposal cost. At \$0.25/kg (\$227.00/ton), this cost is expected to escalate drastically resulting in improved savings in the future.

The savings realized in the ten months of operation are summarized on Table 9. Annual savings have been extrapolated. Maximum potential savings are calculated based upon the plating line operating at full capacity for 6000 hours per year.

The greatest savings have been realized by the chromic acid recovery system. The greater benefits and higher utilization of the chrome system compared with the other systems was due to the fact that hard chrome plating production, not requiring nickel or copper plating, is carried out as well as decorative chrome plating. Nickel sulfate recovery savings were moderate and can increase significantly as production increeases. Low copper plating production resulted in minimal savings. Based on the level of copper plating production, a recovery system could not be justified. However, it should be mentioned that during the initial design stages of the plant, a method to treat or recover the copper effluent had to be included in order for building permit approvals to be granted.

The total annual savings for the first year of operation are calculated to be $13,257.00. As G.G. Buffing's production increases and present costs remain the same, annual savings may reach as high as $60,222.00. In all likelihood, present costs will increase, particularly the sludge disposal costs, resulting in even higher savings. However, even minimal savings are considered acceptable since the installed cost of the recovery system (slightly under $100,000.00 U.S.) was comparable to a destruction/ precipitation type of waste treatment system.

Recommendations

Based upon the experiences of G.G. Buffing, the following recommendations are made to other plants that may be considering a similar approach to reducing or eliminating waste sludge.

1. Proper determination of waste loadings (dragouts) to be recovered by the equipment is important. In G.G. Buffing's case, production and dragout had to be estimated since the plant had not yet been built. Existing plants, especially those with constant production make such dragout determinations easy.

2. Designate at least one person in the plant to be responsible for the system and ensure that he is given the company's support to spend his full time to be trained as the systems are being started up.

. Maintain daily log sheets and forward them on a weekly basis to the equipment manufacturereer for inspection and comment. Such records prove extremely valuable when troubleshooting problems as well as generally monitoring the system's process and economic performance.

4. Should tighter effluent limits need to be met, consider collection and segregated treatment of floor spills and the chromic acid recovery unit effluent.

5. Install sufficient regenerant storage capacity to minimize the need for topping up tanks and reduce the likelihood of running dry.

6. Installation of all the equipment in a common area makes for convenient system monitoring.

7. Prior to startup, clean out all rinse tanks of accumulated solids that might clog filters or ion exchangers.

Conclusions

Chemical recovery systems for chrome, nickel and copper using short bed ion exchange technology have successfully allowed G.G. Buffing to meet effluent discharge limits without producing hazardous waste sludges.

With escalating costs and risks associated with the disposal of hazardous waste metal hydroxide sludges, such an approach in similar electroplating operations should be considered.

1. Patented in Canada, United States and other countries.

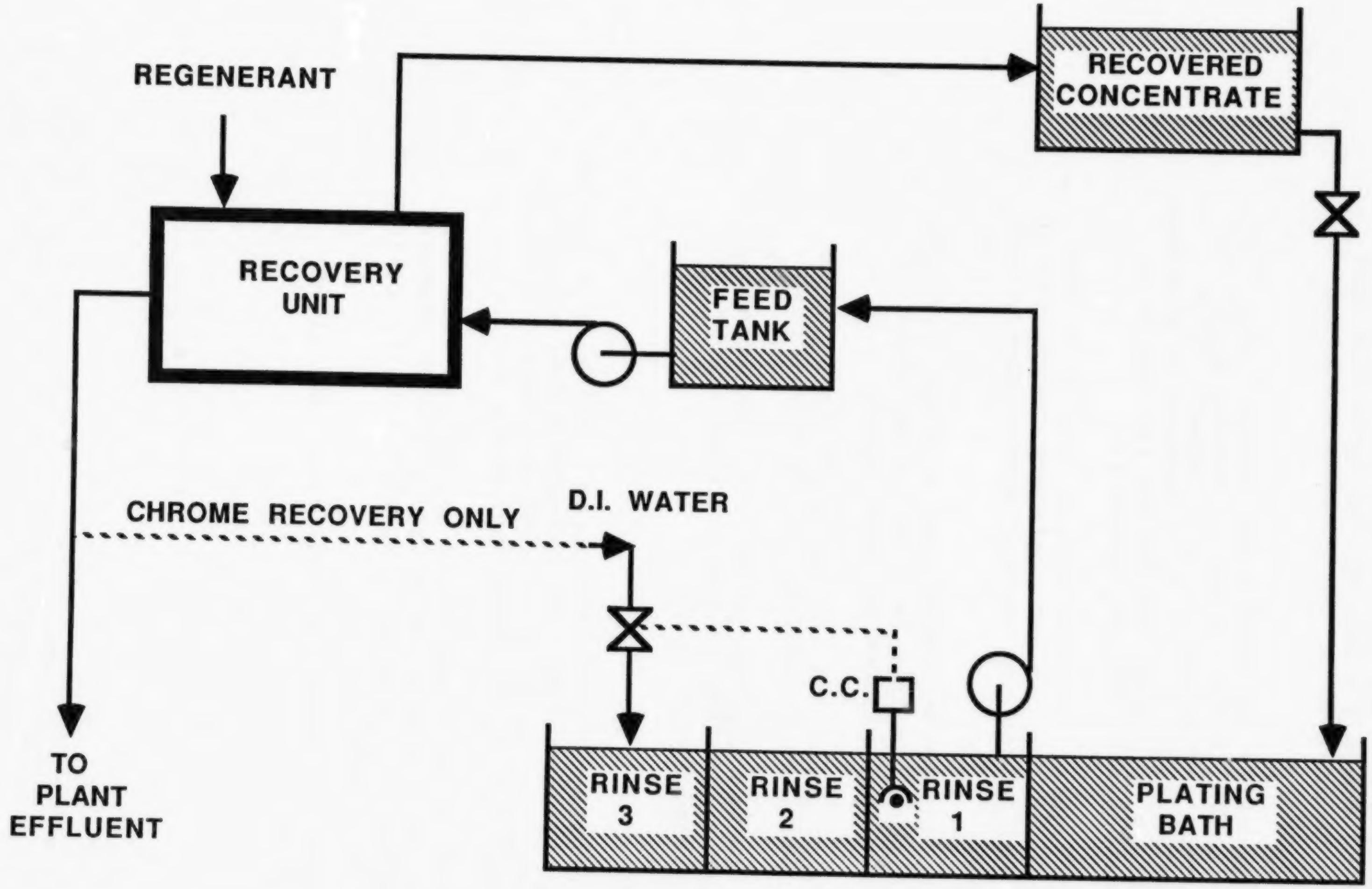
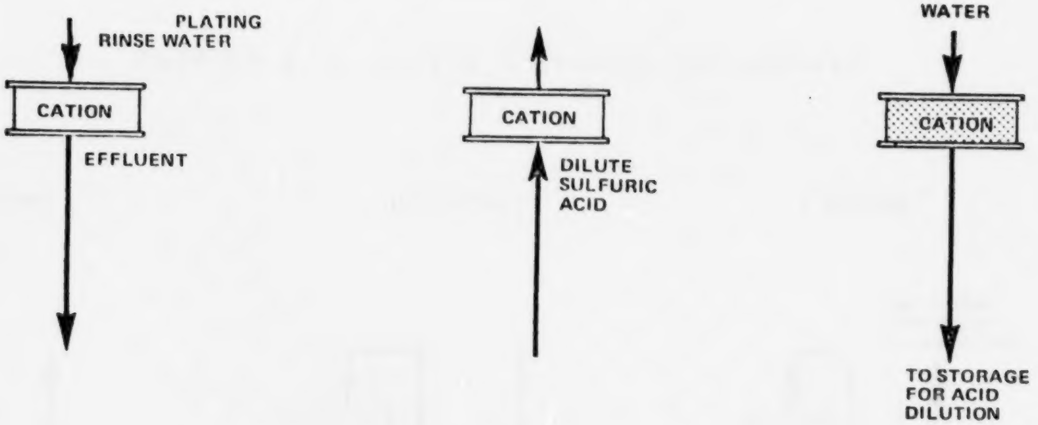

REGENERANT
RECOVERY UNIT
RECOVERED CONCENTRATE
FEED TANK
CHROME RECOVERY ONLY
D.I. WATER
C.C.
TO PLANT EFFLUENT
RINSE 3
RINSE 2
RINSE 1
PLATING BATH

Figure 1 - TYPICAL RECOVERY SYSTEM LAYOUT

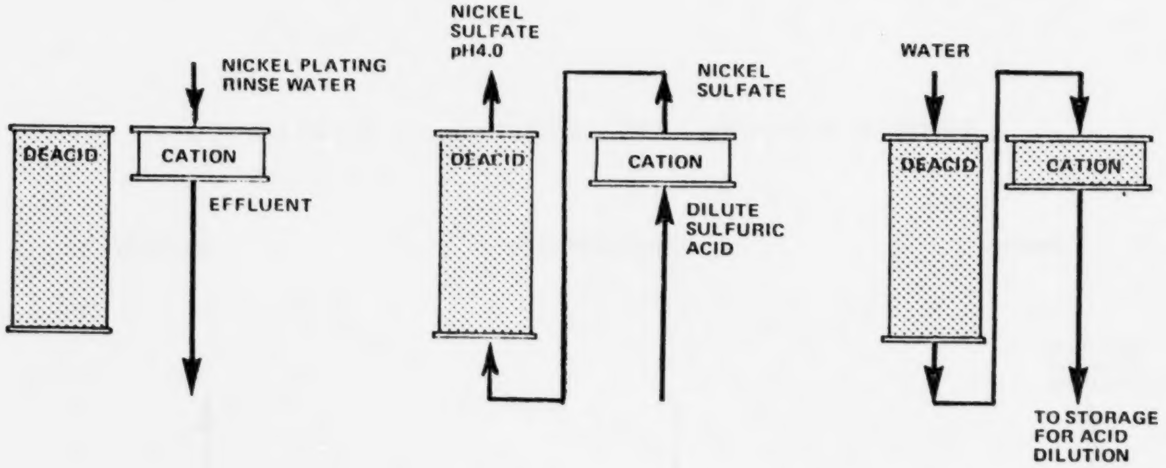

PLATING
RINSE WATER
CATION
EFFLUENT
CATION
DILUTE
SULFURIC
ACID
WATER
CATION
TO STORAGE
FOR ACID
DILUTION

1. Onstream

2. Regeneration

3. Rinsing.

Figure 2 - Copper Salt Recovery Process

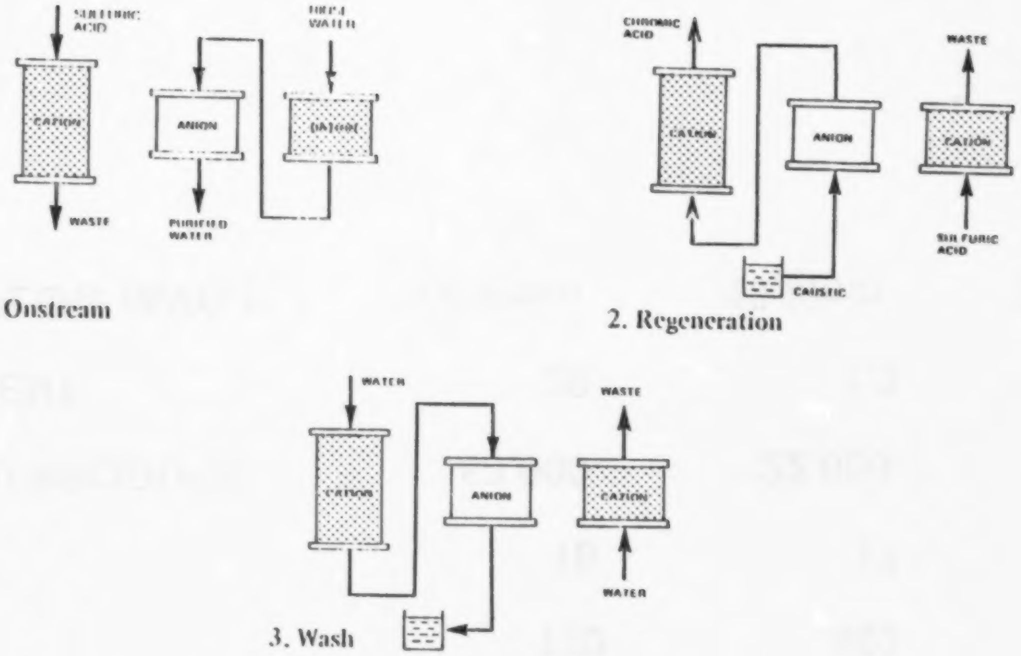

DEACID
CATION
NICKEL PLATING RINSE WATER
EFFLUENT
NICKEL SULFATE pH4.0
NICKEL SULFATE
DILUTE SULFURIC ACID
WATER
TO STORAGE FOR ACID DILUTION

1. Onstream

2. Regeneration

3. Rinsing.

Figure 3 - Nickel Salt Recovery Process


SULFURIC ACID
CATION
WASTE
ANION
PURIFIED WATER
WATER
CATION
CHROMIC ACID
CATION
ANION
CAUSTIC
WASTE
CATION
SULFURIC ACID
WATER
CATION
ANION
WASTE
CATION
WATER

1. Onstream

2. Regeneration

3. Wash

Figure 4 - Chromic Acid Recovery Process

Table 1

RECOVERY SYSTEM PERFORMANCE

(concentrations in mg/l)

	CR	NI	CU
BATH	260,000	84,000	82,000
1ST RINSE	170	460	260
3RD RINSE	10	17	6
RECOVERED PRODUCT	53,000	22,000	35,000
UNIT EFFLUENT	20	1.3	0.9
EFFLUENT FLOW (AVG.)	1.6 l/min	15 l/min	20 l/min

Table 2

FINAL PLANT EFFLUENT (mg/l)

	ACTUAL	LIMIT
Cr	0.2	5
Ni	1.9	5
Cu	1.4	5
Cn	0.1	1
pH	6.8	6-8
flow		35-45 l/min

Table 3

CHROMIC ACID RECOVERY ECONOMICS

(PER KG OF CrO3)

	CONSUMPTION	UNIT COST	$ COST/KG
SULFURIC ACID (93%)	2.8 KG	0.11/KG	0.31
CAUSTIC SODA (50%)	4.3 KG	0.22/KG	0.95
D.I. WATER	173 L	0.54/1000 L	0.09
BARIUM CARBONATE	0.07 KG	0.88/KG	0.06
ELECTRICITY	2 KW-HR	0.05/KW-HR	0.10
TOTAL			$1.51/KG

Table 4

NICKEL SULFATE RECOVERY ECONOMICS

(PER KG OF $\mathrm{NiSO4.6H2O}$)

	CONSUMPTION	UNIT COST	$ COST/KG
SULFURIC ACID (93%)	0.69 KG	0.11/KG	0.07
CAUSTIC SODA (50%)	1.06 KG	0.22/KG	0.23
D.I. WATER	478 L	0.54/1000 L	0.26
ELECTRICITY	1 KW-HR	0.05/KW-HR	0.05
TOTAL			$0.61/KG

G20

Table 5

COPPER SULFATE RECOVERY ECONOMICS

(PER KG OF $CuSO_4.5H_2O$)

	CONSUMPTION	UNIT COST	$ COST/KG
SULFURIC ACID (93%)	1.1 KG	0.11/KG	0.12
CAUSTIC SODA (50%)	1.7 KG	0.22/KG	0.37
D.I. WATER	981 L	0.54/1000 L	0.53
ELECTRICITY	1 KW-HR	0.05/KW-HR	0.05
TOTAL			$1.07/KG

Table 6

CHROMIC ACID WASTE TREATMENT ECONOMICS

(PER KG OF Cr03)

	CONSUMPTION	UNIT COST	$ COST/KG
CHROMIC ACID	1 KG	2.75/KG	2.75
SODIUM BISULFITE	1.5 KG	0.63/KG	0.94
CAUSTIC SODA (50%)	2.3 KG	0.22/KG	0.51
SLUDGE DISPOSAL (30%)	6.6 KG	0.15/KG	0.99
TOTAL			$5.19/KG

NET SAVINGS/KG = $5.19 - $1.51 = $3.68/KG

Table 7

NICKEL SULFATE WASTE TREATMENT ECONOMICS

(PER KG OF $NiSO4.6H2O$)

	CONSUMPTION	UNIT COST	$ COST/KG
NICKEL SULFATE	1 KG	2.80/KG	2.80
CAUSTIC SODA (50%)	0.3 KG	0.22/KG	0.07
SLUDGE DISPOSAL (30%)	1.15 KG	0.25/KG	0.29
TOTAL			$3.16/KG

NET SAVINGS/KG = $3.16 - $0.61 = **$2.55/KG**

Table 8

COPPER SULFATE WASTE TREATMENT ECONOMICS

(PER KG OF $CuSO_4.5H_2O$)

	CONSUMPTION	UNIT COST	$ COST/KG
COPPER SULFATE	1 KG	1.14/KG	1.14
CAUSTIC SODA (50%)	0.32 KG	0.22/KG	0.07
SLUDGE DISPOSAL (30%)	1.3 KG	0.25/KG	0.32
TOTAL			$1.53/KG

NET SAVINGS/KG = $1.53 - $1.07 = $0.46/KG

Table 9

TOTAL SAVINGS

	10 MONTH CYCLE COUNT	RECOVERY PER CYCLE	NET SAVING	10 MONTH TOTAL SAVING	ACTUAL ANNUAL SAVING	MAXIMUM POTENTIAL SAVING
CHROMIC ACID	6572	0.32 KG	$4.34	$9127	$10,952	$15,624
NICKEL SULFATE	1449	0.5 KG	$2.55	$1847	$2216	$38,250
COPPER SULFATE	230	0.7 KG	$0.46	$74	$89	$6348
		TOTAL ANNUAL SAVING			**$13,257**	**$60,222**

REDUCTION OF CHEMICAL USAGE THROUGH THE USE OF COMPUTERS

Donald S. Harrison
CENTEC Corporation
Reston, VA

Introduction

Many electroplaters have purchased and installed wastewater treatment equipment to meet their environmental responsibilities and to comply with regulations. The expense of such systems for the typical shop is significant. Not only is the initial investment cost high, but the annual expense of operation and maintenance is also substantial. The sludge that is produced by such a wastewater treatment system must be hauled away and disposed of at an ever-increasing cost. This trend is making dewatering equipment almost mandatory for many platers.

One factor which increases operating costs beyond those associated with efficient operation is the variability of the wastewater characteristics over time due to the rapidly changing conditions within most plating shops. The inability to adapt to changing conditions is often the reason treatment systems fail to comply with regulations. Variability in the wastewater is often compensated for by reagent addition well beyond the actual rates required for proper performance. This mode of operation is expensive in terms of the cost of chemicals used and the creation of excess sludge. The potential exists to upgrade an existing end-of-pipe treatment system by incorporating a control system capable of proper response to a shifting input.

Development of EPA/MFF Grant

In 1978, EPA investigated the possibility of utilizing advanced microprocessor-based technology as a relatively inexpensive method of upgrading the performance of existing wastetreatment systems. This study identified electroplating wastes as a promising application. It was determined that a full-scale demonstration of the operating cost savings by computer control at an electroplating site was justified.

In 1981, the EPA funded the demonstration under a cooperative agreement with the Metal Finishers' Foundation of Chicago. CENTEC Corporation of Reston, VA was subcontracted to perform the work. Considerable interest was expressed by the electroplating industry because of operating problems experienced with waste treatment systems and the potential benefits of the project.

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Selection of the Demo Site

In order for the project to provide the most beneficial results, the following criteria were established for the selection of the site:

- The site should be a job shop.
- The waste stream whould contain a mixture of metals and include chromium and cyanides.
- The existing wastetreatment system should consist of cyanide oxidation, chromium reduction, pH adjustment, solids separation, and sludge dewatering.
- The wastetreatment system should employ conventional analog instrumentation to avoid the necessity of installing special signal converters.

After consideration of several candidate demonstration sites, Stuart-Olver-Holtz, Inc., a job shop in Rochester, NY was selected as the shop most closely meeting the criteria.

(SLIDE #1)

SOH operates plating lines for the application of copper/nickel/chrome, zinc, cadmium, electroless nickel, annodizing, black oxide, tin, tin/lead, and black chrome finishes. The rinse streams are segregated and collected in three sumps; cyanide, acid/alkali, and chromium. Solutions from the three sumps feed the wastewater treatment system. The treatment consists of 2-stage cyanide oxidation, chromium reduction, pH adjustment, solids settling (rectangular clarifier), and sludge dewatering (centrifuge). The wastetreatment system has been in operation since 1976.

(SLIDE # 2)

All pH and ORP instruments consist of immersible sensor-transmitters, receivers, and analog controllers. The controllers in turn regulate the required chemical addition by adjusting the ratio of ON to OFF time of the chemical feed pumps (DAT TYPE CONTROL). The pH and ORP measurements are recorded on stripchart recorders.

(SLIDE # 3)

STUART-OLVER-HOLTZ, INC.
ROCHESTER, N.Y.

PLATING OPERATIONS

- COOPER/NICKEL/CHROME
- ZINC
- CADMIUM
- ELECTROLESS NICKEL
- ANNODIZING
- BLACK OXIDE
- TIN
- TIN/LEAD
- BLACK CHROME

WASTE STREAMS

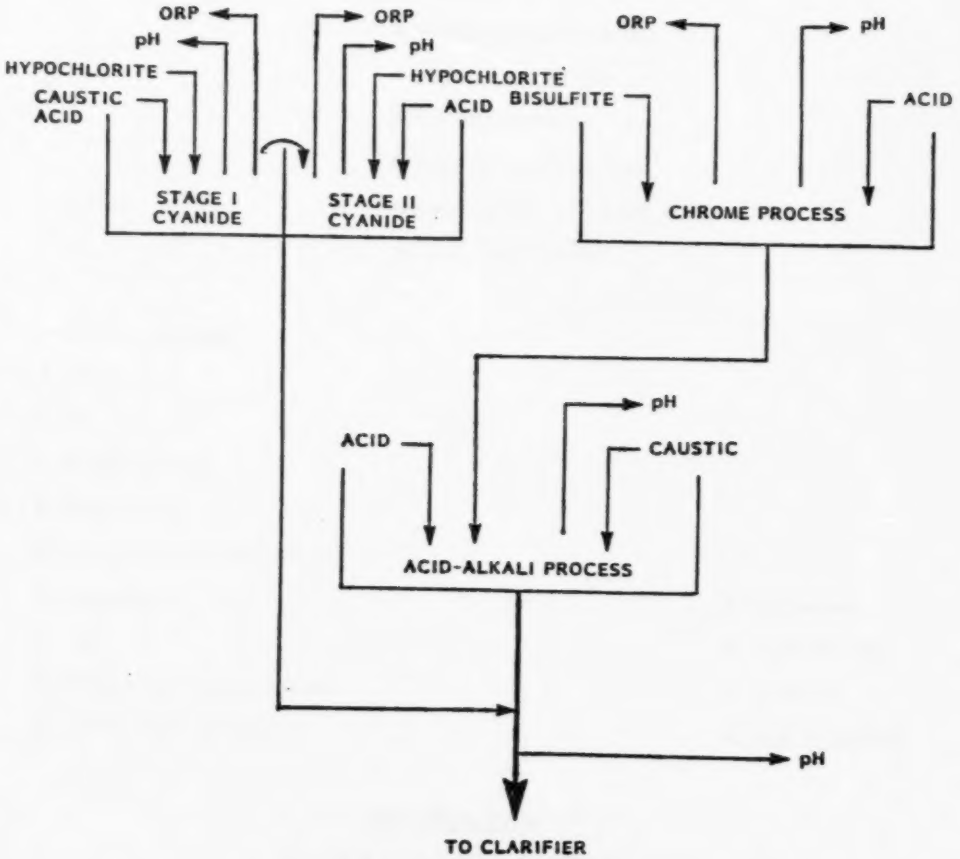
- CYANIDE
- ACID/ALKALI
- CHROMIUM

WASTE TREATMENT

- TWO-STAGE CYANIDE OXIDATION
- CHROME REDUCTION
- pH ADJUSTMENT
- SOLIDS SETTLING
- SLUDGE DEWATERING

SLIDE #1

WATER TREATMENT SYSTEM


ORP
pH
HYPOCHLORITE
CAUSTIC
ACID
STAGE I CYANIDE
ORP
pH
HYPOCHLORITE
ACID
STAGE II CYANIDE
ORP
BISULFITE
pH
ACID
CHROME PROCESS
ACID
pH
CAUSTIC
ACID-ALKALI PROCESS
pH
TO CLARIFIER

SLIDE #2

FUNCTIONAL SPECIFICATIONS

- ACCEPT ALL ANALOG SIGNALS FROM EXISTING TRANSMITTERS
- ECHO ALL ESISTING ALARM FUNCTIONS
- PROVIDE APPROPRIATE OUTPUT SIGNALS TO CONTROL CHEMICAL FEED PUMP

ADDED FUNCTIONS

- ANALOG/COMPUTER SWITCHES FOR EACH CONTROL LOOP
- REAGENT LOW LEVEL WARNING
- TWO-LEVEL WARNING/ALARM CAPABILITY
- LOCAL INDICATION (CRT MONITOR)
- REMOTE INDICATION (CRT MONITOR)
- REMOTE PRINTER-STATUS AND ALARMS

SLIDE #3

Functional Specifications

The functional specifications for the computer controller were developed to give the operator control of the wastetreatment process similar to that which he had with the analog instrumentation. Other features which made the operators job easier were added in hope of gaining acceptance of the computer as his interface with the process. The system was designed to:

- Accept all the analog signals from the existing control panel.
- Monitor all the alarm functions provided on the existing control panel.
- Provide appropriate output signals to control the chemical feed pumps.

These functions essentially replaced the control action of the existing control panel. Additional features were added to:

- Enable switching each control loop between analog and computer control. This feature was provided to avoid loss of control of the treatment system during the startup and troubleshooting phases.
- Provide a low level warning on the treatment chemical storage tanks. These tanks seem to run dry at the most inconvenient time and are a common cause of upsets in the treatment system.
- Provide a two-level warning/alarm system. The first level alerts the operator via a flashing light that a controlled parameter has strayed beyond a preset limit. The second level (alarm) activates an audible alarm. If the alarm represents a potentially dangerous condition, the entire treatment system shuts down until a correction is made. A printed record is provided for all warnings and alarms with the time of occurrence and correction.
- Provide local monitor (CRT) in the control cabinet to continuously display the current values of all controlled variables. A remote CRT in the lab provides a duplicate display. The remote station is equipped with a printer which provides a complete status of the waste treatment system on demand. Warning and alarm conditions are printed when they occur and when corrected.

(SLIDE # 4)

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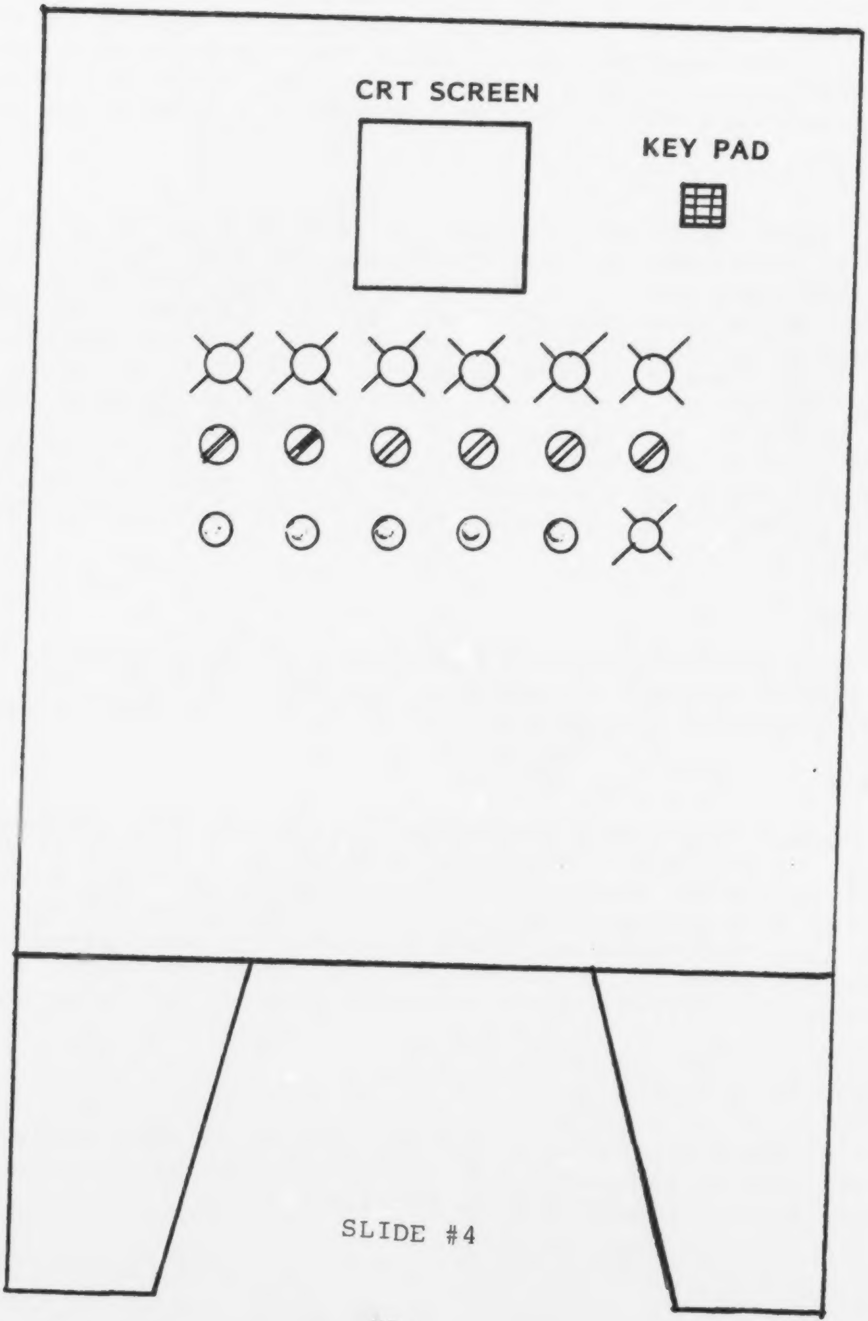
CONTROL PANEL


CRT SCREEN
KEY PAD

SLIDE #4

Hardware

The computer controller was constructed in a 60-inch high by 36-inch wide NEMA 12 enclosure. All hardware necessary for control are located on the front panel. There is a 16-key keypad that is used to enter control and alarm parameters. Six 2-position switches and six lights are used to select and indicate either computer control or conventional analog instrument control. Four pushbuttons complete the controls with ON-OFF, ALARM CANCEL, and SCREEN SELECT functions. The main display is a 9-inch black and white CRT that is behind a plexiglass window.

(SLIDE # 5)

Looking into the interior...on the left side is a terminal strip where all field wiring is terminated. At the top is the CRT. Immediately below this is the card cage that houses the computer boards. Below the computer card cage is a signal conditioner cage with plug-in modules to convert all incoming analog signals to 0-10 vdc for use by the computer. The next two units are optical isolators. One panel handles digital inputs, such as tank level sensing switches; the other handles digital outputs, such as turning on chemical feed pumps. At the bottom are the last four pieces of equipment, the AC distribution box, the DC power supplies, and the modem which drives the remote CRT and printer.

Operation

All interaction between the operator and the process is accomplished through messages on the video screen. The CRT display presents the information on eight different screens.

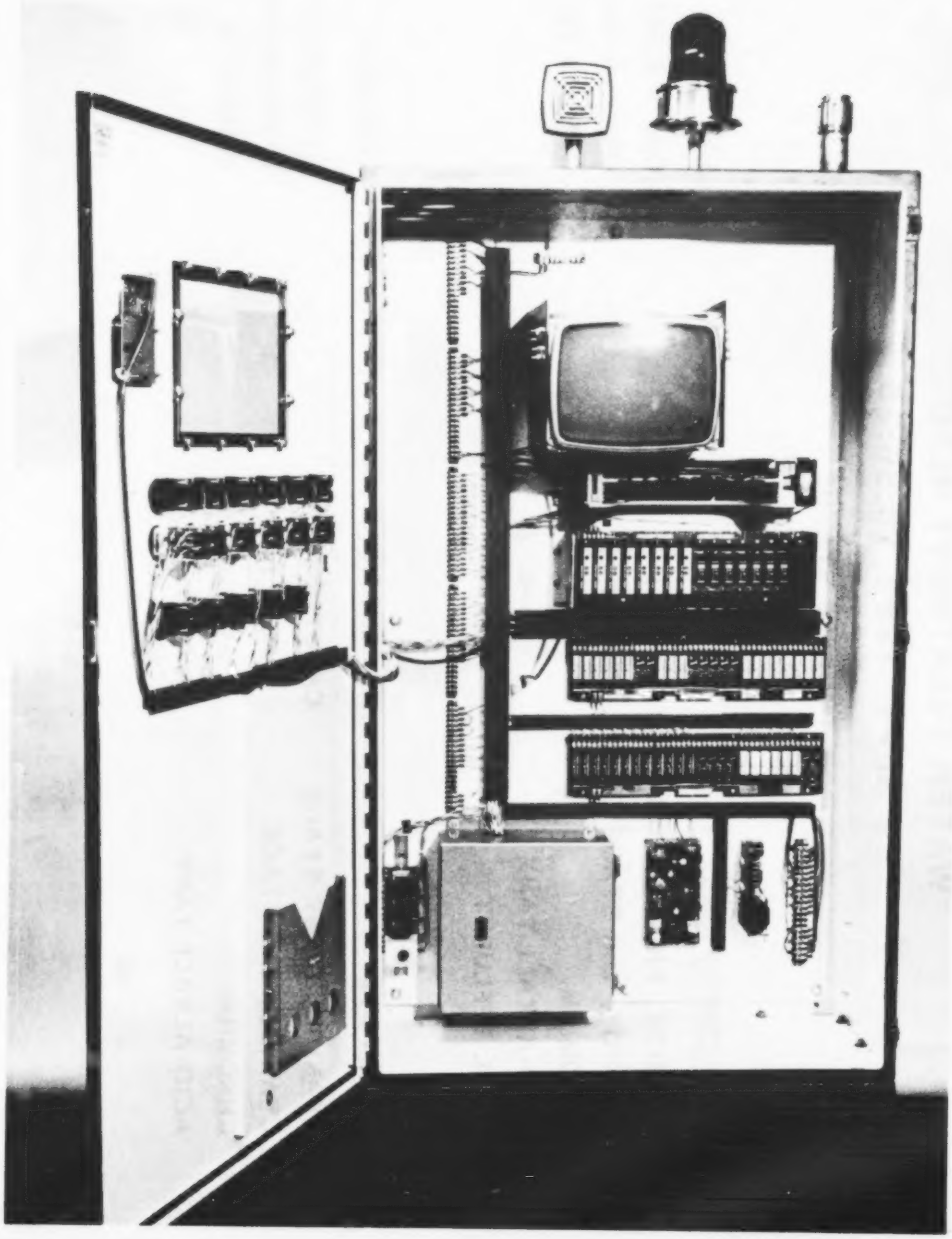
(SLIDE # 6)

Under normal operating conditions Screen #1, the Process Status Display, is visible. The upper half of this screen gives the current values of the pH and ORP measurements. The lower half lists the chemical feed pumps and the duty cycle of each. The screen also indicates the control status of each pump, i.e., whether the pump is on manual control (MAN), is being automatically controlled by the computer (AUTO), or is on analog control (L&N).

(SLIDE # 7)

Screen #2 displays all the warning and alarm conditions. If a warning occurs, the words LOW or HIGH appear in reverse video to replace OK at the appropriate location.

CONSOLE INTERIOR



SLIDE # 5

WATER TREATMENT REPORT
9 SEPT. 1983 16:56:25

PROCESS STATUS

PROCESS CONDITIONS	pH	mV
CYANIDE, FIRST STAGE	10.31	ORP = 0.060
CYANIDE, 2nd STAGE	7.94	ORP = 0.000
CHROMIUM	2.50	ORP = 0.261
ACID-ALKALI TANK	9.58	
FINAL EFFLUENT	9.40	

PUMP OUTPUTS	PERCENT	PERCENT
CYANIDE, FIRST STAGE	CAUSTIC 0.0	HYPOCHLORITE 0.0
CYANIDE, 2nd STAGE	ACID 0.0	HYPOCHLORITE 0.0
CHROMIUM	ACID 0.0	BISULFITE 0.0
ACID-ALKALI TANK	ACID 0.0 CAUSTIC 0.0	

SLIDE # 6

WATER TREATMENT REPORT (Continued)

ALARM STATUS

REGENT LEVELS		SUMPS	SUMP LEVEL	PUMP PRES.
BISULFITE TANK	OK		OK	OK
ACID TANK	OK	CYANIDE	OK	OK
CAUSTIC TANK	OK	CHROMIUM	OK	OK
HYPOCHLORITE TANK	OK	ACID-ALKALI	HIGH	OK
P'ELECTROLYTE	LOW			

DANGEROUS CONDITIONS	pH	ORP
CYANIDE, FIRST STAGE	OK	OK
CYANIDE, 2ND STAGE	OK	
CHROMIUM	OK	OK
ACID-ALKALI TANK	OK	
FINAL EFFLUENT	OK	

SLIDE # 7

Additional screens display current values of manual input parameters and permit the operator to make changes through the keypad.

Remote Equipment

The remote equipment is located in the plant laboratory. It consists of a video monitor that serves as a slave or repeater of the principal video monitor at the console. There is also a printer which serves two functions: logging a full-page status of the wastetreatment system, and recording warnings and alarms each time one is initiated or terminated. Both types of printouts are dated and time stamped.

The lab is also equipped with two pushbuttons: one allows the operator to toggle between the Process Status Screen and the Alarm Status Screen, the other produces a printout of the process status on demand.

Operator acceptance of the system was excellent. At this plant the chemist is responsible for the operation of the waste treatment system. His laboratory is located at the opposite end of the plant from the treatment equipment. The computer saves him many trips to the treatment area to check the operation. The warning and alarm functions allow him to identify the off-normal condition immediately and assess its seriousness.

Results and Conclusions

In order to evaluate the effect of the computer controller on the variability in the plant's effluent, a comparison was made between the effluent analyses for a six-month period prior to installation and the same period under computer control.

(SLIDE # 8)

The figures shown represent the difference between the high and low analyses during the six-month period. With the exception of the Nickel analyses, a considerable reduction in variability was observed.

(SLIDE # 9)

COMPARISON OF EFFLUENT VARIABILITY

PARAMETER	BEFORE	AFTER
PH	3.40	0.80
CN(T)	0.39	0.13
CD	0.05	0.01
CR(T)	0.27	0.00
CU	0.23	0.06
FE	0.70	0.04
PB	0.31	0.13
NI	1.23	1.32
ZN	0.19	0.09

SLIDE # 8

CHEMICAL CONSUMPTION
BEFORE AND AFTER MICROCONTROLLER

ITEM	BEFORE 1-83 to 10-83	AFTER 11-83 to 4-84	PERCENT REDUCTION
SODIUM HYPOCHLORITE	2.30	1.67	27.4
SULFURIC ACID	2.33	1.33	42.9
SODIUM HYDROXIDE	3.20	2.67	16.6
SODIUM BISULFITE	70.0	33.0	52.8

Note: Units are barrels per month; sodium bisulfite is given in pounds per month. Reduction in usage is based on the previous 10 months consumption rate.

SLIDE # 9

A comparison of the treatment chemical usage before and after installation showed a reduction in consumption of 16-52%. These figures admittedly cover a relatively short period of time dictated by the length of the contract. In October 1984, SOH wrote an article for Finishers' Management magazine stating, "six months after installation, savings of $ .98 per 1000 gallons of average monthly water usage were proven due to decreased reagent usage. On an average monthly water usage of 2,500,000 gallons, this savings amounted to almost $2500 per month or $30,000 annually!..."

Second Generation Product

The experience gained from this project has resulted in a product capable of all the functions described earlier and much more.

(SLIDE #10)

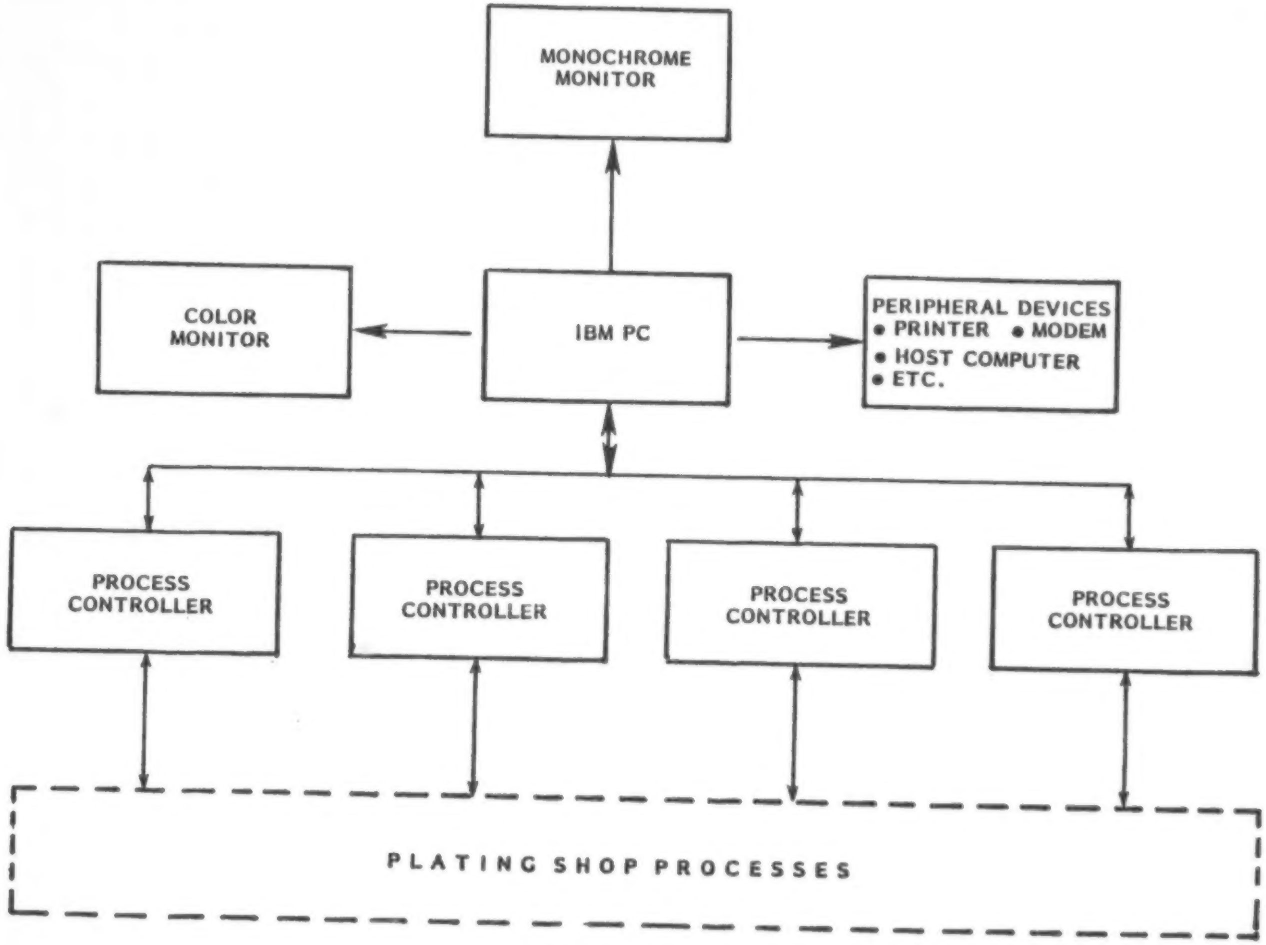
The hardware bears little resemblance to the prototype unit. The computer itself is a standard IBM PC to which a color monitor is connected. The control functions are performed by stand-alone controllers which are microprocessor-based themselves. The computer communicates with any number of controllers throughout the plant. Therefore, the system is no longer limited to the control and monitoring of the wastetreatment system, but can access important process information from the plating shop as a whole.

(SLIDE #11)

Any variable or operation within the plating shop can be monitored by the computer. Parameters are displayed on a color graphic screen specifically designed by the user. Process variables appear in real time, or can be displayed as historical data. Alarm conditions can be indicated by colors as is shown by the Cl_2 and SO_2 blocks indicating that the level of these reagents is low.

Data can be logged and stored for retrieval and analysis at a future time. Spreadsheets and associated graphics provide the user with the ability to examine relationships and trends.

This computer-aided management system is versatile enough that it can be utilized for any of the other tasks within the plant such as accounting, statistical analysis, etc. It was the system's versatility that attracted the attention of major manufacturers of process controllers, including GE, Westinghouse, Honeywell, and Allen-Bradley. With the influence of these companies, the system has evolved into an industry standard for computer-based process control and monitoring.


MONOCHROME MONITOR
COLOR MONITOR
IBM PC
PERIPHERAL DEVICES
• PRINTER • MODEM
• HOST COMPUTER
• ETC.
PROCESS CONTROLLER
PROCESS CONTROLLER
PROCESS CONTROLLER
PROCESS CONTROLLER
PLATING SHOP PROCESSES

SLIDE #10

ELECTROPLATING WASTEWATER TREATMENT

6/19/85

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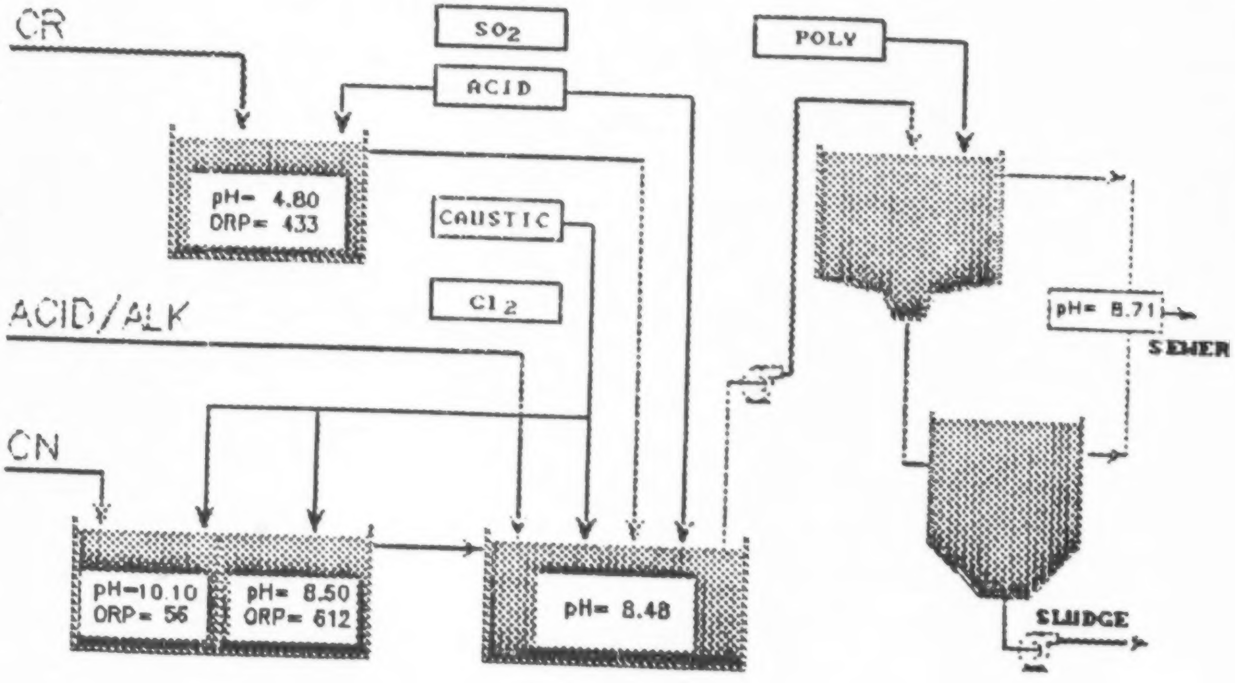
CR
SO2
ACID
POLY
pH= 4.80
ORP= 433
CAUSTIC
Cl 2
ACID/ALK
CN
pH=10.10
ORP= 56
pH= 8.50
ORP= 612
pH= 8.48
pH= 8.71
SEWER
SLUDGE

SLIDE #11

ION EXCHANGE FOR METAL RECOVERY
A DISCUSSION OF THE TRADE-OFFS

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Lancy International, Inc.
Zelienople, Pennsylvania

INTRODUCTION

Ion exchange has been a useful process in metal finishing for several decades. The earliest, and still the most common, application in the United States is for the production of high-purity water. In a quest for recycle of water to minimize discharge and reduce the consumption of limited supplies, the metal finishing industry in Germany began recycling of treated wastewaters through ion exchange systems in the 50's, and it has continued as the predominant practice for handling metal finishing wastes in that country. In view of the extensive application experience, the use of ion exchange for water recycle can be considered a mature technology and well documented.[1,2]

A somewhat younger field of application is the use of either weak acid or chelating cation exchange resins for the removal of traces of objectionable heavy metals from an effluent prior to its discharge to the environment.[1,3] The majority of the commercial experience on this application has been in Germany and Japan where treated effluents, often the regenerant waste from the main deionization and recycle systems, are given a final treatment through such metal-capture systems to give extremely low concentrations of regulated heavy metals in the discharge.

Finally, there has been considerable world-wide interest in the use of ion exchange resins as a medium to transport pollutants from a metal finishing operation to a centralized treatment facility.[4,5] This approach has been attracting increased interest in the USA in connection with the centralized treatment concept. However, none of these approaches is specifically aimed at the recovery of metal values or the avoidance of sludge generation.

For at least twenty years there has been interest in using ion exchange to capture metals from wastewater so they could be recycled or recovered, thus avoiding sludge generation.[1,4,6] However, a number of other technologies compete for such applications, and the trade-offs among them are frequently far from obvious. Regulatory pressure, which disfavors precipitation of metals and sludge disposal, has been increasing dramatically in this country,* making it progressively more important for metal finishers to evaluate their alternatives and choose the most efficient way to minimize sludge generation.

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*Resource Conservation and Recovery Act of 1976 and Amendments of 1984

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Materials capable of accomplishing ion exchange come in a surprisingly wide variety of forms. Defined in the broadest sense, the materials could range from naturally occurring clays and zeolites through specially prepared natural materials (cellulose, peat moss, biomass, etc.) and, finally, to an array of synthetic materials manufactured specifically for the purpose. Comments regarding the applicability of ion exchange in this paper will be focused on the traditional form of the synthetic polymeric materials--beads of a co-polymer consisting of styrene and divinylbenzene. These beads are the familiar ion exchange resin known to most metal finishers. Some of the less familiar or newer forms include liquid ion exchange compounds (ion exchange materials dissolved in an organic carrier fluid which is imiscible with water), fibrous polymers such as polypropylene which can be fabricated into cloth or felt, and hydrophobic plastic membrane materials which can be used to immobilize a liquid ion exchange material. While this paper is focused on traditional ion exchange beads, the reader can determine to what extent the comments may be applicable to other materials.

In addition to various forms, ion exchange can be used in a variety of modes to reduce sludge generation. For example, the ion exchange beads are frequently used to remove cations from chromic acid, purifying it for recycle to a chrome plating operation. In a totally different approach, the beads can be used for a sorption process known as acid retardation[7] to capture and recycle free acid to a process such as aluminum anodizing, avoiding the need to discard and waste treat the entire process solution. However, the most widespread commercial application, and the focus of this paper, is the use of cation exchange resin to capture metal ions from a waste stream to allow their recycle or recovery. There are two ways that sorption of metal cations on a resin can be an important step in recovery or recycle. The first is to transfer the metal ions from one chemical matrix into a different one, more favorable for recovery. For this purpose, the process can be applied to either dilute or concentrated waste materials. The second type of application is to collect the metal ions from a dilute wastewater and transfer them into a relatively concentrated solution of metal salts from which the metal can be recovered, or the metal salts recycled to an originating process bath. Most of the commercial applications in metal finishing are in the second category.

IN-HOUSE RECYCLE OF METAL SALTS

At first glance, return of the metal salts carried out of a process seems like the most elegant way to avoid waste treatment and sludge disposal. In fact, to the extent that the metal salts can be returned, it is the most desirable route since it avoids the need to find a market for a by-product, and since the salt form of the metal, as purchased by the metal finisher, is invariably more valuable than the metal itself. Unfortunately, as discussed in other publications[8,9,10] there are two important reasons why return of metal salts is not a cure-all approach.

1) Many of the baths used in metal finishing, and containing high concentrations of dissolved metal, are discarded on a regular basis because they steadily gain metal content in use. Unless a regeneration process is used on such a bath, return of the metal salt in the drag-out will simply accelerate the need for its discard. Examples are pickles, bright dips, etches, chemical milling solutions, and chromate conversion coating baths.

2) The major electroplating baths which use soluble anodes (zinc, nickel, copper, tin, cadmium, etc.) can accept some return of the metal salt lost to drag-out, but recycle of 100% is not practical because the anodes tend to dissolve more rapidly than the metal deposits at the cathodes. Therefore, without the purging effect of drag-out, the concentration of metal would tend to steadily climb.

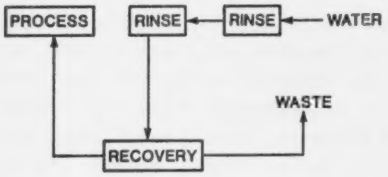
These points notwithstanding, direct recycle of metal salts will continue to play an important role in reducing wastage and sludge production from metal finishing shops. In those cases where it is applicable, the optimum approach will be to directly recycle as much as possible, and either waste, sell, or electrolytically recover that portion of the metal that cannot be recycled to the originating process.

Alternative Technologies

Ion Exchange is one of a group of technologies which have found commercial application in recycling metal salts. The others having fairly extensive commercial application are evaporation, reverse osmosis, and electrodialysis. A brief discussion of each will assist in evaluating trade-offs. For the sake of this discussion, it is assumed that the process to be recovered is followed by two rinse tanks. As will be seen later, the availability of multiple rinse tanks can have important bearing on the applicability of certain tehcnologies, but we are using the two-rinse model here to allow each technology to be evaluated on a comparable basis. In some cases, the two rinse tanks might be piped as a counterflow arrangement and connected to the recovery equipment as shown in Figure 1.

Figure 1

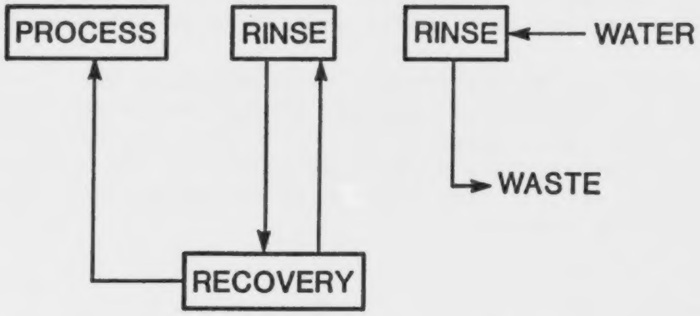
COUNTERFLOW RINSE MODEL



In other cases, it will be more desirable to use the first rinse step as a "recovery rinse"--often flowing at a relatively slow rate--and the second tank as a freely flowing water rinse as shown in Figure 2.

Figure 2

RECOVERY RINSE MODEL



Evaporation - Salts are recovered from the rinsewater by heating it to drive off the water as vapor. Since the water is being moved away from the salts by an energy-intensive phase change, it is imperative to have the flow of water minimized. Typically, this approach is characterized by an arrangement as shown in Figure 2, operating at a relatively low flow rate. Therefore, the recovery rinse is rather concentrated in the valuable salts, and losses to waste are relatively high. On the other hand, the concentration of the product is almost unlimited.

Reverse Osmosis - Since it is less energy intensive, higher flow rates are typically used to give better capture efficiency for the metal. Unfortunately, the RO product cannot be highly concentrated because of inherent limitations of the technology. This can be a serious restriction on its applicability unless supplemental evaporation is provided. It is noteworthy that both evaporation and RO return essentially all of the constituents in the drag-out to the originating process. This can be either an advantage or a liability, depending on the circumstances of the particular case.[9]

Electrodialysis - In this case, ionized salts are moved out of the recovery rinsewater through ion exchange membranes, under the influence of an electromotive field. Since the conductivity of the recovery rinse must be reasonably high, the losses to subsequent rinsing would typically be higher than reverse osmosis or ion exchange, but lower than evaporation. The concentration of the product is quite high, being limited only by the amount of water transported through the membranes with the ions. Thus, the volume of the product is seldom a limitation on its ability to be returned.

Ion Exchange - Unlike the other methods, ion exchange is almost totally unaffected by the dilution of the water being fed to the recovery unit. Rinsing as depicted in Figure 1, with relatively high flow rates, can be used effectively. This method can have an extremely high capture efficiency since discharge of metal from the ion exchange column can be as low as hundredths of a milligram per liter. Product concentration is rather low by comparison to evaporation and ED, although typically higher than achievable with RO.

The major trade-offs among these four technologies are summarized qualitatively in Table I.

TABLE I
COMPARISON OF TECHNOLOGIES

	Evap.	RO	ED	I Ex
Feed Conc.	High	Low	Med.	Very Low
Product Conc.	Very High	Low	High	Med.
Capture Efficiency	Low	High	Med.	Very High
Energy	High	Med.	Low	Very Low

SOME TRADE-OFF FACTORS

Advantages

Without question, a very important advantage of ion exchange is its ability to extract essentially all of the metal from a relatively dilute feed stream. This makes it the only candidate for certain applications as discussed subsequently. It also means that it is the only one of the four technologies discussed above which can produce an effluent water suitable for discharge without further treatment. Finally, ion exchange tends to be at the low end of the capital and operating cost spectrum for a given loading rate; i.e., pounds of metal per hour.

Disadvantages

The two primary disadvantages with ion exchange are the dilute product which results and the fact that it is a chemically driven process. The dilute product derives from the fact that the resins are a gel of the styrene/divinylbenzene co-polymer, with a significant percentage of their weight made up of water. As such, they are subject to osmotic pressure differentials which develop when a chemical solution outside the resin bead has a much higher concentration than that inside. This limits the concentration of acid which can be used to regenerate the cation exchange resin, thus restricting the concentration of metal salt which can be obtained from the process. Under ideal conditions, concentrations as high as 50 grams/liter of metal can be obtained, but in practice the product is more likely to contain 15-30 grams/liter of metal. Innovative engineering approaches on the equipment used to conduct the process are needed to get the higher concentrations, and these tend to add complexity, control problems, and operating and maintenance labor requirements.

Since ion exchange is chemically driven, it increases the consumption of chemicals by the plant and the quantity of salt in the water being discharged. Of more immediate concern in regard to direct recycle of the product stream is the excess acid which is virtually inevitable. In many cases, the free acid will prevent recycle to the originating process and schemes to separate it from the desired metal salt again add cost, complexity, and operating and control requirements.

Control is an important factor in using ion exchange since breakthrough of the metal being captured occurs rather abruptly once the resin bed is saturated. Compared to the other technologies, this means that metal loss will go up very sharply once breakthrough is exceeded, whereas metal losses with the other technologies would be increased only slightly if control and operator attention were sub-optimal. Because of this, most commercial installations avoid using the resin bed to exhaustion. Unfortunately, this makes it impossible to pace the regenerant acid to the requirement, inevitably resulting in even more excess acid in the product. This problem could be eliminated with an instrument that would reliably detect breakthrough of metal ions. There has been steady progress in developing rugged, reliable instruments for this purpose, but even the best of them are relatively delicate and sophisticated for many metal finishing shop environments. Obviously, if ion exchange is being used to produce a high-quality effluent for discharge, the importance of detecting breakthrough is even more important than if it is being used simply as a recovery tool. In addition, close control over the pH of the feed to the exchanger is necessary since lower pH tends to reduce capacity and performance, while a pH slightly on the high side will precipitate metal and plug the exchanger or its filter.

As a Waste Treatment Process

The ability of ion exchange to produce high-quality discharge water has led to extensive consideration of the technology as a combined treatment and recovery approach. As the example discussed later will illustrate, this happy circumstance can occur under the right conditions. Unfortunately, they are relatively rare. Most metal finishing shops have a combination of metals in the discharge water which all but eliminate the possibility of economical metal recovery. In addition, the regulated heavy metals are quite often found in a variety of process baths at varying concentrations, so that segregation of one or a few rinse tanks will not bring a plant into compliance. An example would be zinc or cadmium found in the alkaline cleaner, acid dip, and chromate dip on a zinc or cadmium plating line. Another would be chromium and/or nickel found in the alkaline cleaner, acid dip, parts stripper, and rack stripper in a decorative plating plant. A final example would be the copper found in numerous process baths in a printed circuit shop. Clearly, installation of an ion exchange system on the rinse following the main plating process will not be an assurance that the total plant effluent will meet regulations. Conversely, installation of a metal capture system on the total plant effluent will essentially rule out recycle of metal salts to the main plating process which would be the only point it could have utility.

ATTRACTIVE APPLICATIONS

When multiple rinse tanks after a process are simply out of the question, ion exchange may be a very attractive way to capture metal ions before the water goes to treatment. In rare cases it might be attractive to fully deionize the water and recycle it back to the tank, but this will seldom be optimalfor two reasons:

1) A single rinse tank cannot remove the drag-out film sufficiently to justify the use of ultrapure water.

2) The use of a chelating cation exchange resin will minimize the amount of excess acid needed to regenerate the exchanger.

Two cases will serve to illustrate where a single rinse tank and capture by ion exchange may be the best choice for metal recovery. The first would be an existing finishing shop in an urban location where space for additional rinse steps cannot be obtained. The second would be a shop handling very large pieces, and thus having large rinse tanks, but relatively light loadings. The expense and space required for additional rinse steps cannot be justified by the improved efficiencies with any of the other recovery technologies.

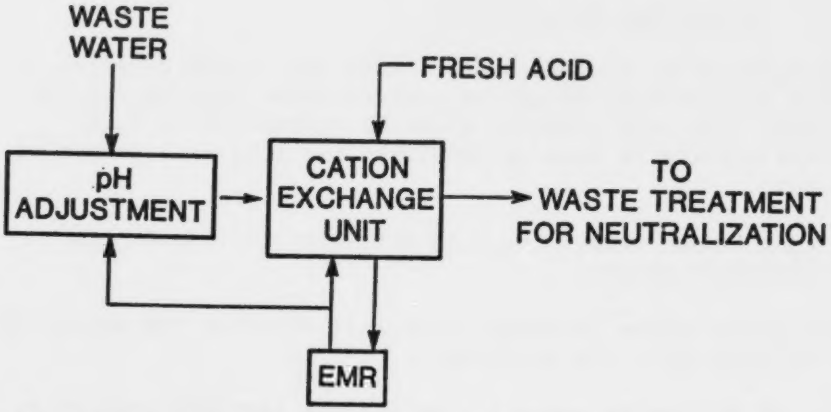
A different situation exists where rinsing requirements are extremely critical. Such situations frequently occur where the cost of a product or its reliability are overriding considerations and rule out normal economic trade-offs. In such cases, manufacturing engineers may insist upon extremely high rinsewater flow rates and/or may prohibit any use of recycled water. As in the case mentioned above, these situations may favor the use of ion exchange even if it is not the most efficient and economical approach.

A Non-Return Approach

Where return of metal salts to the originating process tank does not look attractive, ion exchange can be linked with electrolytic metal recovery (EMR)--sometimes referred to as electrowinning--to good advantage. The two primary disadvantages of ion exchange discussed earlier--dilute product and excess acid--are of no concern in this scheme. Figure 3 is a simplified depiction of the arrangement.

Figure 3

ION EXCHANGE LINKED WITH ELECTOLYTIC RECOVERY

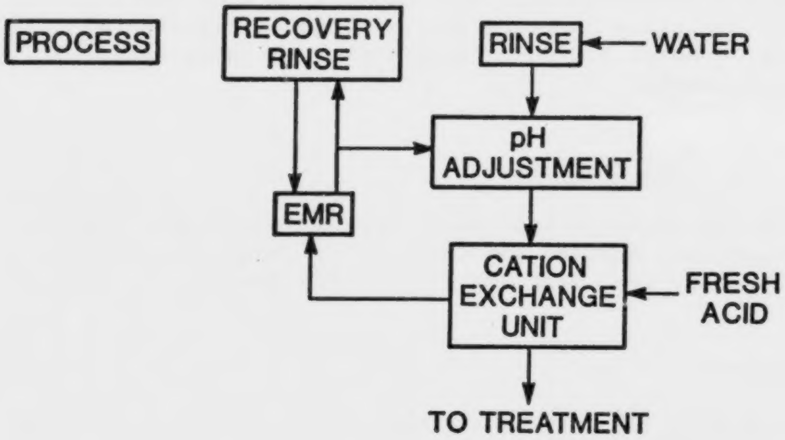


The metal-depleted wastewater would require pH adjustment prior to discharge. Control would be critical to minimize discharge of metal, since the breakthrough is rapid once the resin is exhausted. Sulfuric acid would be used to regenerate the exchanger and the product from the exchanger would go to EMR where the metal would be deposited as slabs for sale as a by-product, and the acid content would be re-formed. The excess acid in the depleted liquor from the electrolytic cell can be used to do the first stage of regeneration on subsequent cycles of the exchanger. Since this liquor still contains some metal, fresh acid is needed to complete the regeneration cycle. The excess acid leaves the system by being neutralized with the incoming raw waste and passed through the ion exchanger, so that the metal content is not lost.

The inefficiency in this scheme is that a portion of the metal being recovered is constantly recycled, requiring that the exchange equipment be oversized. A more efficient scheme would use electrolytic recovery for the majority of the loading--for instance, 80-90%--and ion exchange to capture the small amount remaining in a subsequent rinse. Such an approach is illustrated in Figure 4.

Figure 4

OPTIMIZED I.EX./EMR COMBINATION



In this scheme, only a tiny fraction of the total amount of metal being recovered gets recycled through the exchanger. It is important to note that both Figure 3 and Figure 4 are simplified diagrams, and that holding tanks and control instruments are needed to make a practical system. Obviously, the extra cost and complication of such a system is undesirable if one of the more straightforward approaches discussed earlier can give acceptable performance.

The scheme in Figure 3 can be especially attractive for complexed or chelated metal if the ion exchange material will remove metal from the waste. In this case, expensive waste treatment methods normally used for such difficult streams can be avoided.

It should also be noted that laboratory testing is highly recommended for any application of ion exchange which has not been done on a commercial scale with exactly the same process chemicals. The entire chemical matrix of a waste stream can influence exchange rates, capacities of the ion exchange resin, and quantity of regenerant acid needed.

Centralized Recovery

Combining portable ion exchangers with EMR at a centralized recovery facility can provide an attractive option where the geographic locations of a number of small sources of a recoverable metal make it logistically feasible. It is important to note that the capacity of the resin for metal can be case specific, and in many cases lower than the average values published in the literature. A range of 0.5 to 2.5 pounds of copper per cubic foot of resin is not unusual, depending on both the pH control of the feed stream and the entire chemical matrix involved. When at the lower end of this range, the trucking costs can become a significant factor unless the distances are short. Also, it is important to note that this arrangement is likely to be feasible only for the more valuable and recoverable metals, and when they are in a segregated condition. As discussed earlier, this is a much different concept than using portable ion exchange cannisters to attempt to bring an entire metal finishing shop into compliance with effluent discharge requirements.

TWO EXAMPLES

Work on two projects during the past year will serve to illustrate how ion exchange can be advantageously applied and some of the important considerations for laboratory test work and engineering design.

Electroless Nickel Waste

This client had approximately 500 gallons per day of discarded electroless nickel plating bath. In addition, there were smaller quantities of electroless cobalt nickel plating solution (less than 10 gallons per day average) and a treatment system was needed to produce an effluent under 1 mg/liter of nickel. Treatment by conventional means proved problematic on the concentrated waste because of the presence of high concentrations of complexing agents for nickel. Laboratory and pilot-scale test work indicated that a proprietary electrolytic cell* would effectively and efficiently remove nickel from the initial concentration of 5-7 grams/liter down to the range of approx. 150 mg/liter. Table II indicates the results of several attempts to further treat the depleted liquor from the electrolytic cell.

TABLE II

TREATABILITY TESTS
ELECTROLESS NICKEL DUMP
Ni - 3.9 grams/liter

Method	Effluent Concentration mg/l
1. Electrolytic Recovery	140
2. Hot Lime/Hydrosulfite on #1	25
3. Sorption Filter on #2	8.0
4. Excess Sulfide and Sorption Filter on #1	3.1
5. Sodium Borohydride Treatment on #1	32.0
6. Chelating Ion Exchange Resin on #1	less than 0.25

*Patent Pending

The chelating ion exchange resin showed considerable promise as the most effective approach, particularly since the loadings were relatively light, and the nickel could be recycled to the electrolytic cell after regeneration of the ion exchanger.

The work for this client was a continuation of numerous tests done over several years on many different proprietary electroless plating baths. Some results from these various tests will serve to illustrate key factors to be considered in applying the technology. Guidelines provided by resin manufacturers for conventional applications may not apply with difficult or concentrated waste streams. In the case of electroless nickel bath dumps, the high concentration of soluble complexing agent in the waste provides competition for the nickel ions, and alters the sorption kinetics from what would be typically experienced in dilute conditions such as rinsewater.

Most applications of ion exchange resin use the material in a continuous reactor which takes the form of a relatively tall column. As waste moves downward through such a column, the upper layers become saturated first and a moving zone is produced which can be considered the actual reaction zone or wave front for the adsorption process. The length of this reaction zone is dependent on the kinetics of the actual sorption process as well as the flux rate or throughput of waste (often expressed as gallons per minute per square foot). The test results in Table III illustrate the significance of column configuration on both removal performance and the capacity of a given quantity of resin to hold metal.

TABLE III

BED DEPTH VERSUS LOADING CAPACITY
Ni Results in mg/liter

Bed Volumes	0.5 ft. Column	2.0 ft. Column
10	0.10	0.05
20	0.50	0.10
30	0.10	< 0.05
40	0.20	< 0.05
50	0.10	< 0.05
60	1.00	< 0.05
70	2.10	< 0.05
80	8.00	< 0.05
90	--	< 0.05
100	--	0.30
110	--	5.00

For this test, a proprietary nickel bath was diluted to a nickel concentration of approximately 150 mg/liter. The pH was adjusted to 9.0 and the adsorption runs were conducted at 1 gallon/minute per cubic foot of resin, so that the total contact time between waste and resin was the same in both tests. The short column had an internal diameter of 7/8 inch and a resin bed height of six inches. The deeper had an internal diameter of 3/8 inch and a bed depth of 24 inches. Each column had an identical quantity of ion exchange resin. Using 1.5 mg/liter as the unacceptable discharge level indicates that the same quantity of resin in a taller column had a capacity for about 70 percent more metal than the shorter column. In a full-scale system, the bed depth would normally be considerably greater, reducing the significance of the capacity effect, but this test clearly illustrates the presence of the reaction zone and the importance of using proper laboratory techniques and interpreting the results for engineering purposes.

The significance of pH control is illustrated by another series of tests using the liquor from the electyrolytic cell mentioned earlier. These tests were isotherms in which a measured quantity of resin, calculated to be approximately the amount needed to totally sorb the nickel contained in a measured quantity of waste was stirred over a period of hours. The resin had been previously put in the sodium form, and each of the samples for the test had its pH adjusted with sodium hydroxide. Figure 5 plots the adsorption of nickel over time at the various pH levels.

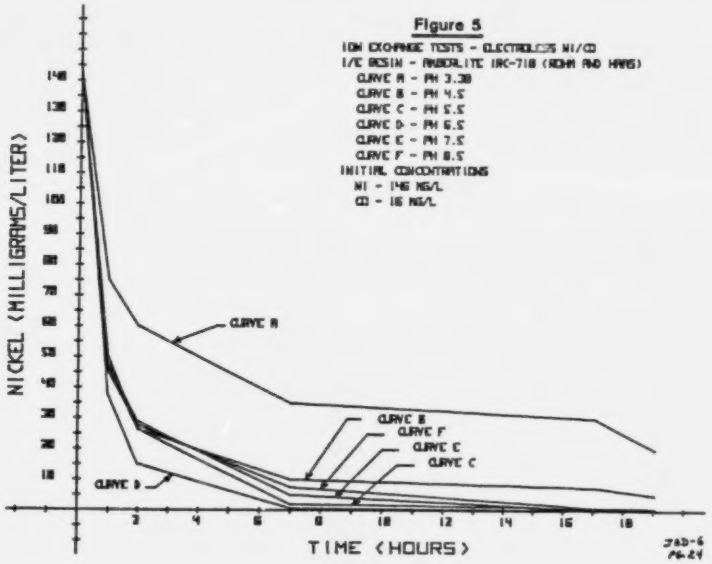


Figure 5

The plots illustrate the significance of pH, both on capacity of the resin to hold metal and on the rates at which adsorption occurs. For this application, pH 6.5 is optimum, and is fortunately a practical level since the complexing agent keeps the nickel soluble. Unfortunately, in many applications, the metal will be insoluble at an optimum pH, so the waste must be kept acidic (typically 4.0-4.5), thus reducing both resin capacity and adsorption kinetics.

Sizing of an exchanger and the flow rate at which waste can be applied are dependent on the adsorption kinetics. Resin manufacturers give guidelines for typical applications, and the range of hydrdaulic loadings is normally between eight bed volumes per hour and forty volumes per hour. Figure 6 illustrates the significance of this factor.

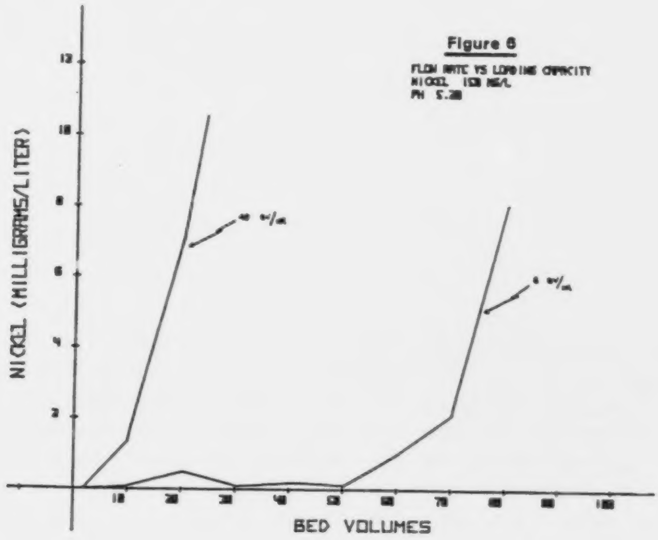


Figure 6

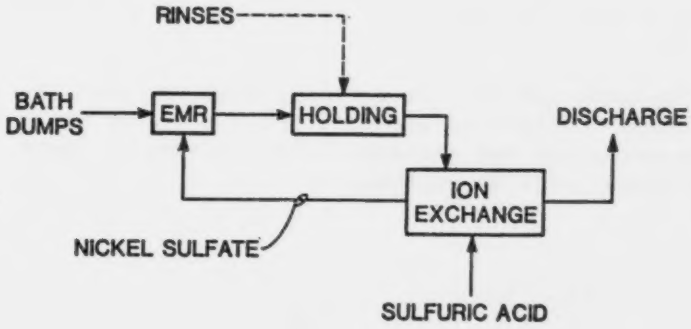
FLOW RATE VS LOADING CAPACITY
NICKEL 150 MG/L
PH 5.20

A proprietary electroless nickel bath was diluted to a final concentration of 150 mg/liter and run at the resulting pH of 5.2. The column for these tests was 24 inches deep. As can be seen, the lower end of the typical range of hydraulic loadings is necessary for this condition, and the effect is even more pronounced if the bath is run full strength without dilution.

The end result of the treatability work for this client is a compact treatment system illustrated as a simplified flow diagram in Figure 7.

Figure 7

ELECTROLESS NICKEL SYSTEM



In this particular case, rinsewaters were not to be included since they were adequately handled through an existing treatment system. Since the system would handle relatively constant volumes of bath dump with essentially the same composition, metal detection on the effluent from the exchanger was considered unnecessary. As indicated in the sketch, rinsewaters could also be incorporated into the system, but they are likely to be far more variable in composition, so that a metal detector for breakthrough from the column would be needed to get optimization of the loading cycles. The physical system consisted of an electrolytic cell with approximately 100 square feet of cathode surface and a pair of ion exchange reactors, each containing approximately 1.6 cubic feet of chelating ion exchange resin. One column is to be on stream and the other regenerated and held in standby.

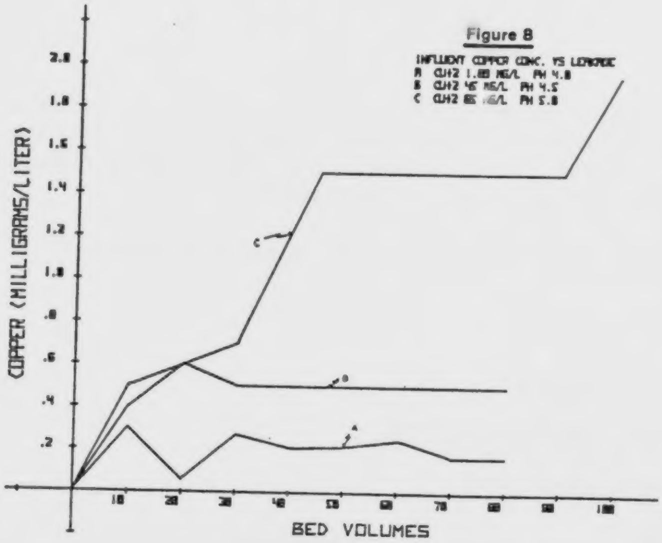
Printed Circuit Board Waste

This client had an existing waste treatment system which handled the total effluent from the wet processing operations. Since it was originally a prototype rather than a production-run shop, the treatment system was set up to be capable of handling virtually any chemistry and incorporated ferrous sulfate, sodium hydrosulfite, and lime additions to a continuous and batch treatment system. Over the years, production rates increased so that chemical consumption, sludge disposal, and loadings on the treatment system all became prohibitive.

Laboratory treatability work was done on selected samples, with the aim being to handle all copper-containing wastes through a system using both electrolytic metal recovery and ion exchange. The sources of waste containing complexed copper were as follows:

- Alkaline cleaner dumps and rinses
- Electroless copper dump and rinse
- Etcher rinses
- Solder strip rinse

For the lab testing, samples of each of these wastes were blended in appropriate proportions so as to illustrate a fairly wide range of ratios of electroless copper dump to rinsewater. The copper concentration in the resulting wastewater ranged from less than 2 mg/liter to approximately 65 mg/liter. Figure 8 shows three different wastes run through a 24-inch-deep column of chelating ion exchange resin at a rate of 1 GPM per cubic foot.



In these tests, the resin was in the sodium form, but subsequent testing showed essentially the same loading rates and capacities with the resin in the hydrogen form.

The scheme contemplated for handling these wastes would route all of the complexed or chelated wastes through the ion exchange system and have the regenerant waste from the exchanger processed in an electrolytic metal recovery cell. The same cell would also remove copper from high-strength, non-chelated copper sulfate wastes. To illustrate the manner in which the regenerant waste from the exchanger can be split into high-strength and low-strength streams, the following table lists the copper concentration in various fractions leaving the column.

TABLE IV

REGENERATION OF ION EXCHANGER

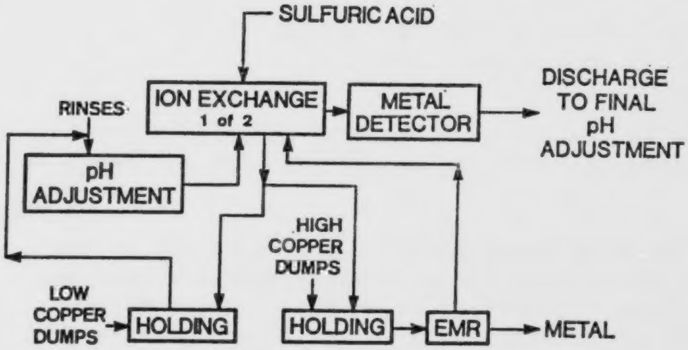
Cycle	Bed Volumes Throughput	Copper - g/l
Backwash	1.0	0.03
Regeneration	0.2	7.2
- 10% by weight H_2SO_4	0.2	24.3
	0.2	15.1
	0.2	6.0
	0.2	5.3
Rinse	1.0	0.01
	1.0	0.003

Approximately 80 percent of the copper is eluted in the first 60 percent of the volume of the acidic waste from regeneration. This quantity would be recycled to the electrolytic metal recovery cell, and the remainder would be neutralized and recycled back through the ion exchanger.

Figure 9 is a simplified block flow diagram of the treatment scheme contemplated.

Figure 9

PRINTED CIRCUIT SHOP SYSTEM


SULFURIC ACID
ION EXCHANGE
1 of 2
METAL DETECTOR
DISCHARGE TO FINAL pH ADJUSTMENT
RINSES
pH ADJUSTMENT
HIGH COPPER DUMPS
LOW COPPER DUMPS
HOLDING
HOLDING
EMR
METAL

In this case, a metal detector is mandatory because of the relatively high variability of the feed stock to the exchanger. The net result of employing this scheme is that approximately 65 pounds per week of copper will be recovered from the wastewater as high-grade by-product slabs. The cost of the recovery system cannot be justified on the basis of copper recovery, but when savings for treatment chemicals and sludge disposal are included, the overall picture is an attractive return on investment.

SUMMARY

Ion exchange is a flexible process which can be useful in recovering metals from metal finishing wastewaters under certain conditions. The outstanding advantage of the process is its ability to capture essentially all of the metal fed to it even when the feed stream is very low in metal concentration. On the other hand, the two major disadvantages are that the product is relatively low in metal concentration and contains appreciable free acid. Also of importance in certain cases is the increase in total dissolved salts which must be discharged from a plant using ion exchange.

The two major disadvantages mentioned above can be troublesome when attempting to recycle metal salts from rinsewaters to an originating process bath, but they are of little consequence when the process is linked with electrolytic metal recovery.

Although cascading two technologies adds cost and complexity, the trade-off can be favorable for special situations. Examples include cases where complexing agents interfere with metal removal by traditional waste treatment and the ion exchange process can serve the dual function of capturing the metal for recovery and producing an effluent suitable for discharge.

ACKNOWLEDGEMENT

The authors wish to acknowledge the invaluable assistance of Jay Dwyer who generated some of the data used in this paper and assisted in its interpretation and presentation.

REFERENCES

1. Hartinger, L., Taschenbuch der Abwasserbehandlung, Carl Hanser Verlag Munchen Wien, 1977.

2. Weiner, R., "Total Recovery, the Final Solution of Waste Problems in the Metal Finishing Industry," presented at International Water Pollution Research Conference, Stockholm, Sweden, January, 1975.

3. Waitz, W. H., "Ion Exchange in Heavy Metals Removal and Recovery," Amber-Hi-Lites No. 162, Rohm & Haas Company, Fall, 1979.

4. Yagishita, A., et al, "Recycling in the Japanese Electroplating Industry," Proceedings of 72nd Annual Technical Conference of the American Electroplaters' Society, Detroit, Michigan, July 15-18, 1985.

5. Wahl, K. L., "Spulwasserbehandlung als Dienstleistung," Galvanotechnik, 71 (1980) Nr. 7, pp. 721-728.

6. Kunin, R., "Ion Exchange for the Metal Products Finisher," Products Finishing, April, 1969, pp. 66-73, and May, 1969, pp. 71-79.

7. Brown, C. J., Davy, D., and Simmons, P.J., "Purification of Sulfuric Acid Anodizing Solution," Plating and Surface Finishing, Jan., 1979, pp. 54-57.

8. Lancy, L.E., "Accumulation of Organic Impurities from Recovery of Nickel Plating Drag-out," Metal Finishing, April, 1983, pp. 27-32.

9. Steward, F. A., Baker, T.E., Resnick, F.J., "Electrodialysis for the Recovery of Nickel Salts, "Proceedings of 72nd Annual Technical Conference of the American Electroplaters' Society, Detroit, Michigan, July 15-18, 1985.

10. Steward, F. A., McLay, W. J., "Waste Minimization," Metal Finishing, September, 1985, pp. 55-57.

SLUDGE REDUCTION THROUGH USE OF THE HIGH DENSITY SLUDGE PROCESS

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Abstract

The High Density Sludge (HDS) Process is an improvement to conventional hydroxide precipitation in which a controlled amount of precipitated sludge is recycled back into the precipitation process to produce a pumpable sludge that concentrates to 20-40% in a clarifier and has excellent dewatering properties. Sludge from the HDS process can be further dewatered to solids concentrations in excess of 50% and overall sludge treatment and disposal costs can be reduced by 20% to 50% using the HDS process.

Laboratory pilot work on chrome bearing electroplating waters showed that the HDS process, in conjunction with either ferrous sulfate or sodium bisulfite reduction of hexavalent chrome, will produce a sludge with solids concentrations of 20%-25% in the clarifier underflow. This sludge was further dewatered to solids concentrations of 36% to 41% by vacuum filtration and 43% to 52% by a filter press.

Introduction

The need to reduce the volumes of sludge generated in the treatment of metal bearing wastes is more crucial now than it has ever been. With the cost of sludge disposal increasing at a rapid rate, technologies for reducing the volumes of sludge generated are becoming economic necessities. While it is advantageous to prevent solid waste generation by recovery and recycle wherever possible, there will always be waste streams that will have to be chemically treated and will form a solid waste. In those instances, it would be beneficial to utilize processes that minimize the cost of treatment and the amount of sludge that must be disposed of.

One such technology to reduce the volumes of sludge generated in the precipitation of metal wastes is the High Density Sludge (HDS) process. In this patented process, sludges with a solids concentration of 20-40% can be produced in the precipitation process. These solids concentrations can be increased to over 50% by further dewatering.

The HDS process was originally developed in the mid 1960's by Bethlehem Steel researchers to reduce sludge disposal costs in the treatment of acid mine drainage. Use of the HDS process produced sludges with solids concentrations of 20-40% compared to the 1-5% solids achievable with conventional neutralization. By reducing sludge volume by an average factor of 15, significant savings in sludge handling and disposal costs were achieved.

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Subsequently, the HDS process was applied to the treatment of steel plant pickling wastes. Currently, there are 3 plants using the HDS process to treat a total of 2,500 gpm of metal bearing wastewaters in addition to the 9 plants treating acid mine drainage.

More recently, the process has been applied to the treatment of various heavy metals wastewaters containing combinations of zinc, zinc-cyanide, lead, chrome, copper, nickel, and cadmium. This paper will discuss the treatment of wastewaters from a chrome plating operation.

Application of HDS Treatment to Electroplating Wastewaters

As described by Herman (1), the HDS process can be used to treat metal-bearing wastewater and produce a sludge containing up to 50% solids. A block diagram comparison of the HDS and conventional neutralization processes is presented in Figure 1. The key differences between HDS and conventional neutralization treatment are that 1) a controlled volume of the settled sludge is recycled back to the neutralization process and 2) the recycled sludge is mixed with the alkaline agent in a sludge reactor prior to the neutralization and solids separation steps. This controlled recycle and sludge reaction promotes the precipitation of dissolved metals onto recirculated particles so that a denser sludge can be formed.

The HDS Process is particularly suitable for treating the acidic metal bearing wastewaters that are generated in the electroplating and metal finishing industries. It can work on both batch and continuous processes and can be easily retrofitted into many existing facilities. The advantages of HDS in treating these waters are as follows.

- Reduction of sludge volume

  As opposed to sludge solids concentrations of 1 to 5% that are achieved in conventional processes, HDS treatment can consistently produce sludges with solids concentrations of 20 to 40%.

- Reduction of sludge treatment costs

  In addition to reducing the amount of sludge produced in the neutralization process, the sludge produced by HDS treatment dewaters faster than sludges produced by conventional neutralization.

- Improved treatment of mixed metal solutions

  The HDS process also has advantages in treating mixed metal solutions. In tests with solutions containing copper, cadmium, nickel, lead, and zinc, the HDS process was able to reduce all of the soluble metal concentrations to less than 0.1 mg/l in a single precipitation step at a single pH (Reference 1). With conventional waste treatment processes, several pH adjustments and precipitation steps are usually required for complete precipitation of all metals.

- Improved pH control

  The continuous recycle of the alkaline sludge back into the sludge reaction step helps to buffer swings in pH caused by changes in process stream flows. This helps to provide better pH control for the precipitation reaction.

HDS Treatment of Chrome Plating Wastewater

To supplement existing treatment facilities and to meet new discharge regulations, Bethlehem Steel is currently designing an HDS facility to treat chrome bearing rinse waters from a Tin Free Steel strip plating line and a tin plate chromating operation. This facility will treat up to 1200 pounds per day of chrome.

The design for this plant is based on the results of laboratory testing of the HDS process in conjunction with both ferrous sulfate and sodium bisulfite reduction of hexavalent chrome. Based on our past experiences, laboratory data can be used to accurately design a full scale facility.

Laboratory HDS System

A bench scale HDS system, complete with chemical feed system, pH control, sludge thickening and sludge recycling, was used to conduct this test program. For bisulfite treatment (shown in Figure 2), sodium metabisulfite is added to the chrome bearing wastes in Reactor C. The reduced chrome solution flows into Reactor B where a mixture of lime and recycled sludge is added from Reactor A. The treated solution then flows to a thickener or clarifier where a clean effluent is discharged and sludge is either recycled to Reactor A or discharged for dewatering and disposal.

In the ferrous sulfate case (shown in Figure 3), spent pickle liquor from steelmaking operations is added to the chrome bearing wastes in Reactor C. The reduced chrome solution flows into Reactor B1 where a portion of the recycled sludge is added to control the pH and to promote the formation of a dense ferric hydroxide sludge. The effluent from B1 then flows to Reactor B2 where the combination of lime and recycle sludge from Reactor A is added to precipitate chrome in the form of a dense sludge. The effluent from B2 flows to a thickener/clarifier for solids/liquid separation.

The feed water for this system was a combination of (1) chromate passivation rinsewaters from a tin plate line and (2) rinses and miscellaneous chrome bearing wastes from a continuous chrome plating line. Hexavalent chrome concentrations in the HDS influent averaged 120 mg/l and total chrome concentrations averaged 140 mg/l.

Results and Discussion

Results of test work conducted between October 1984 and March 1985 showed that HDS treatment in conjunction with either bisulfite or ferrous sulfate reduction could successfully remove chrome from the wastewaters and produce a dense sludge. Due to lower sludge production, the bisulfite approach was chosen for the full scale facility. From this w[illegible] we have developed the following observations.

Effect of HDS Treatment on Chrome Removal ---

Given proper hexavalent chrome reduction, soluble chrome in the treated effluent can be reduced to the same levels that are achievable with conventional alkaline neutralization. In both the ferrous sulfate and bisulfite reduction cases, hexavalent chrome was reduced to less than 0.05 mg/l and total soluble chrome was reduced to less than 0.1 mg/l.

Suspended chrome in the effluent from HDS treatment will be a function of the total suspended solids in the effluent and the percentage of total suspended solids that is chrome. In the ferrous sulfate case, suspended chrome was 11% of total suspended solids while in the sodium bisulfite case, chrome was 30% of total suspended solids.

Since clarification and thickening requirements for the HDS process are similar to those for conventional neutralization, the size of the clarifier/thickener will depend on the flow rates and solids loadings.

Effect of HDS Treatment on Sludge Density ---

As the HDS sludge recirculation process operates, the solids concentration in the thickener increased from typical concentrations found in conventional neutralization systems (1-5%) to concentrations typical of HDS treatment (20-40%). Table 1 shows the sludge density buildup as a function of operating days for several runs of both ferrous sulfate and bisulfite reduction treatment.

In both cases, sludge concentrations of up to 40% solids were achieved. Since the nature of HDS solids is significantly different than conventional hydroxide solids, the sludges were still fluid and pumpable at these concentrations. In steady-state operation with subsequent sludge dewatering, a sludge density of about 25% will be optimal. After the desired sludge concentration is reached, the system can be maintained in equilibrium by proper control of sludge wasting (disposal).

Sludge Dewatering of HDS Sludge ---

Vacuum filtration, belt press filtration and pressure filtration were evaluated in the laboratory for further sludge dewatering. In Table 2, the results of these tests are compared with typical dewatering of metal hydroxide sludges.

Starting with an initial solids concentrations of about 25%, vacuum filtration produced a sludge with final solids concentrations of 36% for bisulfite-reduced and 42% for ferrous iron-reduced sludge. Filtration rates for HDS sludge were 3 times faster than rates for conventional hydroxide sludge. Belt press filtration produced a 46% cake for ferrous iron-reduced sludge.

Pressure filtration produced the driest final cakes. Final solids concentrations of 43% and 52% were achieved for the bisulfite-reduced sludge and the ferrous iron-reduced sludges respectively.

Impact on Sludge Treatment and Disposal Costs ---

The use of the HDS process can result in significant savings in sludge dewatering and disposal costs. For example, for facilities without sludge dewatering equipment, increasing the sludge concentration from 5% to 25% solids will reduce the amount of sludge disposed of by 80%.

For facilities with existing sludge dewatering equipment, significant savings can also be achieved with use of the HDS process. For example, a local electroplating shop using bisulfite reduction and a filter press for dewatering is now getting a filter cake with 20% solids. The 43% cake achieved with the HDS sludge would reduce the amount of sludge to be disposed of by over 50%. Additionally, with faster filtration rates, cycle times will be shorter, reducing operating costs or increasing effective capacity.

For facilities requiring new dewatering equipment, the HDS process saves on both capital and operating costs. In the Sparrows Point application, where about 2500 lbs/d of dry solids will be generated, the costs of vacuum filtration and pressure filtration of HDS sludge have been estimated and compared to costs for dewatering conventionally generated sludge (Table 3). For both vacuum filters and filter presses, the capital costs and the total annual sludge treatment and disposal costs are significantly lower with HDS treatment than with conventional precipitation techniques.

For a two shift operation, a 4 ft^2 vacuum filter is required to dewater HDS sludge to 35% solids compared to a 90 ft^2 filter which would dewater conventional sludge to 25% solids. Because of reduced operating costs and lower ultimate sludge volume in the HDS case, total annual sludge treatment and disposal costs are $126,000 for HDS sludge compared to $190,000 for conventional sludge.

If pressure filtration is chosen for dewatering, both capital costs for a filter press and ultimate sludge volume will be less if HDS treatment is used. Total annual sludge treatment and disposal costs using a filter press are estimated at $136,000 for HDS sludge and $169,000 for conventional sludge.

Conclusion

The High Density Sludge Process is an effective heavy metal treatment technology that reduces the volume of sludge generated in electroplating operations. By incorporating the HDS process into new systems or by retrofitting it in existing facilities, significant savings in sludge treatment and disposal costs can be achieved.

References

1. Herman, S. T., "The High Density Sludge Process: An Improved Technology for Hydroxide Precipitation of Heavy Metals," presented at the EPA/AISI Symposium on Iron and Steel Pollution Abatement Technology for 1983, Chicago, OH, October 1983.

Table 1 Solids Concentration in HDS Sludge as a Function of Operating Time

	Final Solids Concentration in Clarifier Underflow			
	Bisulfate Reduction		Ferrous Sulfate Reduction	
Day	Run 1 %	Run 2 %	Run 1 %	Run 2 %
1	--	5	--	--
2	7	17	4	3
3	16	21	9	3
4	13	28	12	5
5	13		16	9
6	18		19	14
7	11		--	19
8	15		28	22
9	12		41	23
10	35		30*	23
11	38		48	
12	49			
13	38*			
14	34*			
15	41			

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* Reduction in sludge solids concentration due to bleeding sludge from the system.

Table 2 Final HDS Sludge Density after Dewatering

	Percent solids in sludge			
	Before Dewatering	Vacuum Filtration	Belt Press	Filter Press
Ferrous sulfate reduced sludge	25	41	46	52
Bisulfite reduced sludge	23	36	--	43
Typical performance on conventional, metal hydroxide sludge *	3	25	30	35
Chrome sludge from local electroplating shop conventional neutralization				21

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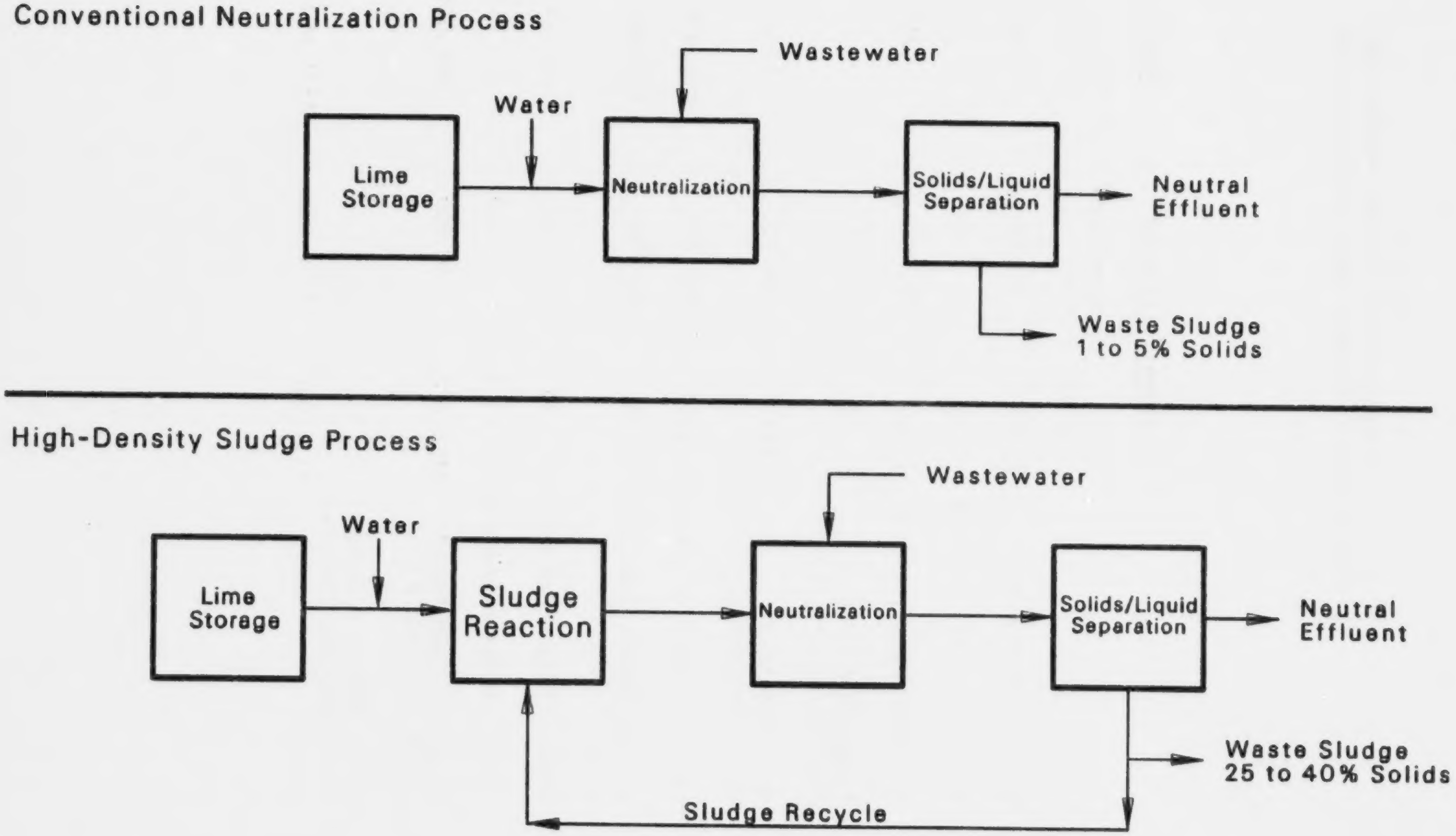
* From "Environmental Pollution Control Alternatives: Sludge Handling, Dewatering, and Disposal for the Metal Finishing Industry, October 1982, USEPA

Table 3
Comparison of Sludge Dewatering
HDS Sludge vs Conventional Neutralization Sludge

	Vacuum Filtration		Pressure Filtration	
	HDS Sludge	Conventional Sludge	HDS Sludge	Conventional Sludge
Lbs dry solids/day	2,500	2,500	2,500	2,500
Initial sludge conc, %	20	3	20	3
Initial Volume, gals	1,250	10,000	1,250	10,000
Filtration Rate (gal/ft/hr)	20	7		
Size Required (2 shifts/day)	4ft2	90ft2	15ft3	25ft3
Capital Cost	$25,000	$50,000	$30,000	$40,000
Annual Dewatering Cost (incl. dep)	$18,000	$40,000	$42,000	$43,000
Final Sludge Density, %	35	25	40	30
Final Sludge Weight, t/d	3.6	5.0	3.1	4.2
Disposal Cost, $/yr ($100/ton, 300 d/y)	$108,000	$150,000	$94,000	$126,000
Total Annual Sludge Treatment and Disposal Cost	$126,000	$190,000	$136,000	$169,000

Figure 1. Block Diagram Comparing Conventional Neutralization and the High Density Sludge Process



Conventional Neutralization Process

High-Density Sludge Process

Lime Storage
Water
Neutralization
Wastewater
Solids/Liquid Separation
Neutral Effluent
Waste Sludge 1 to 5% Solids
Lime Storage
Water
Sludge Reaction
Neutralization
Wastewater
Solids/Liquid Separation
Neutral Effluent
Waste Sludge 25 to 40% Solids
Sludge Recycle

Figure 2
Schematic Diagram of the High-Density Sludge Plant
For Treatment of Chrome-Bearing Wastewaters ,
Chrome Reduction with Bisulfite

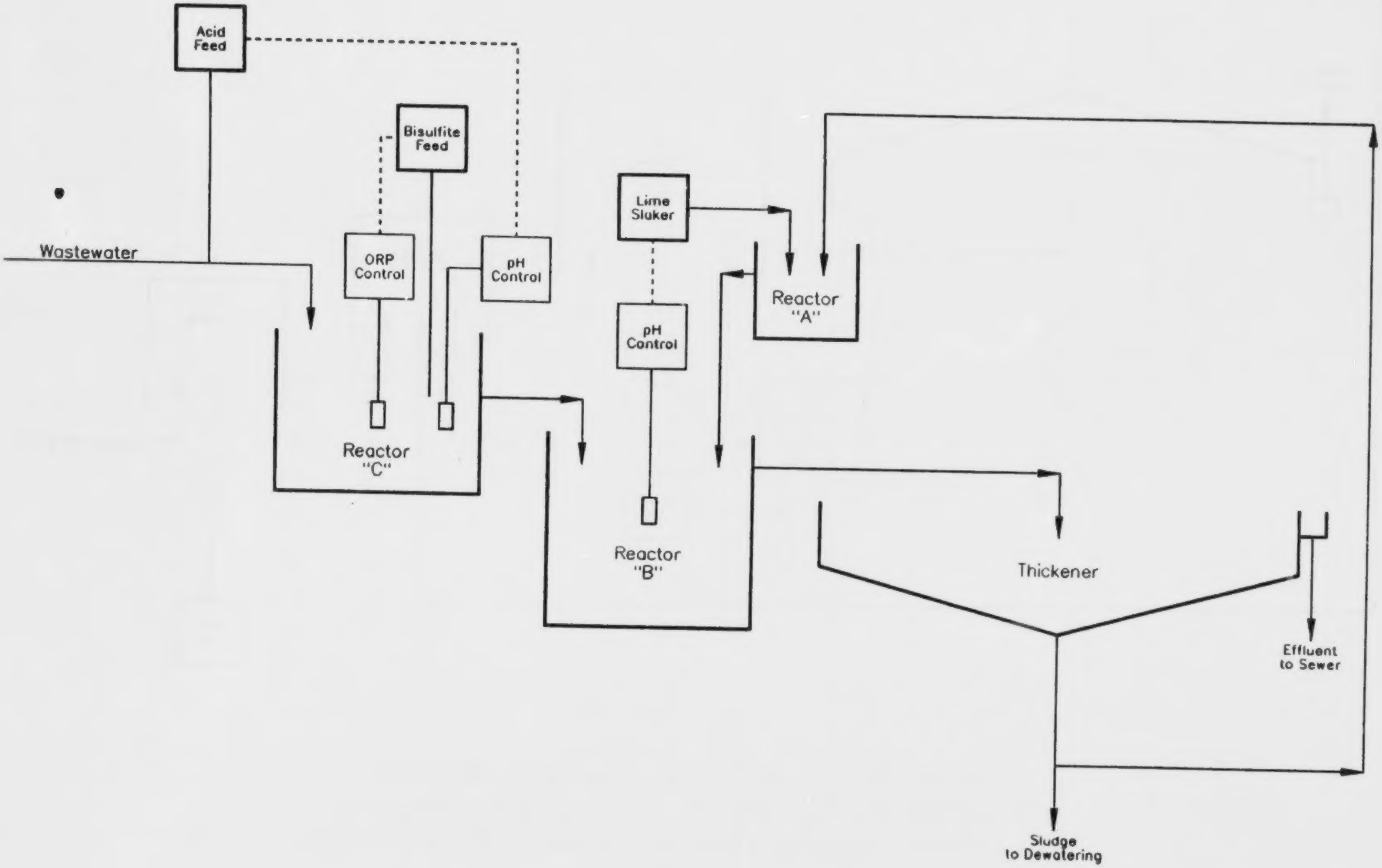
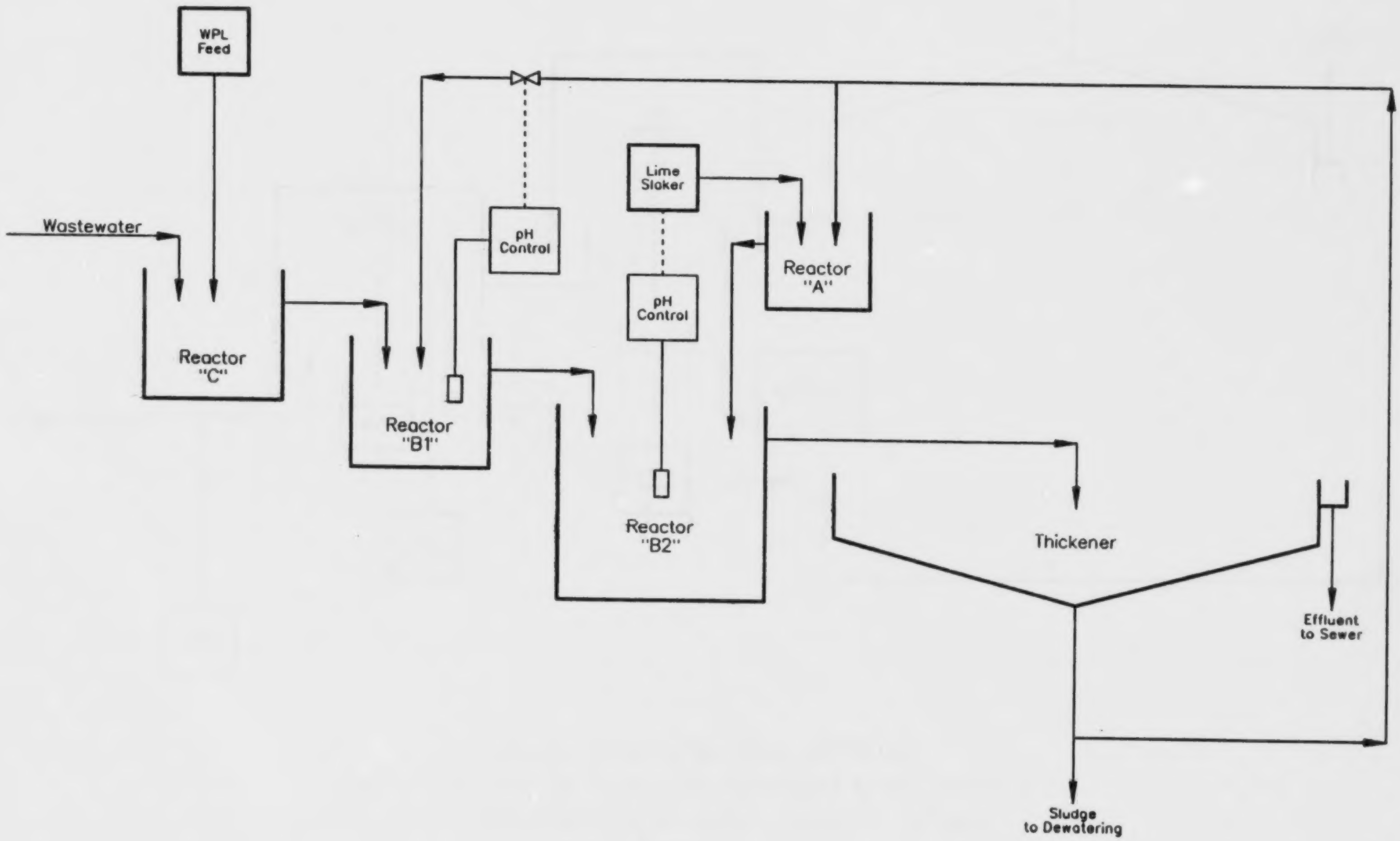

Acid Feed
Bisulfite Feed
Wastewater
ORP Control
pH Control
Reactor "C"
Lime Sluker
pH Control
Reactor "A"
Reactor "B"
Thickener
Effluent to Sewer
Sludge to Dewatering

Figure 3
Schematic Diagram of the High–Density Sludge Plant
For Treatment of Chrome–Bearing Wastewaters
Chrome Reduction with Spent Pickle Liquor


WPL Feed
Wastewater
Reactor "C"
pH Control
Reactor "B1"
Lime Slaker
pH Control
Reactor "A"
Reactor "B2"
Thickener
Effluent to Sewer
Sludge to Dewatering

AMMONIACAL ETCHANT REGENERATION
AND
COPPER RECOVERY

"An Alternative State-of-the-Art Process"

Carlos Rivera
Digital's Printed-Wiring Board Facility
San German, Puerto Rico

Gary DeClue
Digital's Technology Center
Andover, MA

A chemical process has been successfully implemented in a production printed-wiring board facility which recycles spent ammoniacal etchant and allows for removal of dissolved copper as electrolytic copper cathodes. Recycled etchant is brought back to specification by addition of relatively small quantities of replenisher. This installation has been in full operation for over 10 months with no process downtime or loss in process performance.

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BACKGROUND

The San German PWB facility, inaugurated by Digital in 1972, is located in the western part of the Island of Puerto Rico.

One of the challenges faced in this remote yet technically complex facility was the disposition of spent ammoniacal based etchants. Over the past 10 years, these materials had been transported via tank trucks across the island and then loaded onto a ship bound for an eastern United States port for recycling.

This procedure, while adequate at the time of implementation, was recently judged to be a potential risk due to increased regulations mandated by the DOT and EPA. An alternative to this procedure was established with the implementation of a solvent extraction system utilizing the Mecer Process*.

DISCUSSION

Compliance with the present and future environmental regulations will in many ways dictate the flexibility of chemicals used in the printed-wiring board (PWB) industry of tommorrow. Efforts to meet this challenge have caused significant changes in assessing how process performance is measured. While both Quality and Yield are still very important metrics of performance to the product manufactured, other legal implications of process performance must also be appreciated.

Following are some questions used to assess process performance:

a. Are the chemicals and materials used in the process hazardous?

b. What controls are in place to protect the employee and how do they work?

c. How much material is consumed in this process?

d. What is to be done with the waste materials generated?

e. What will you do with these materials tommorrow?

---

* Sigma Engineering AB, Goteborg, Sweden

The successful implementation of this **Chemical Process** in our PWB facility in San German, Puerto Rico has proven to be a reasonable, cost effective solution utilizing metal recovery and etchant reuse that meets these environmental and process performance challenges of the future.

ADDITIONAL BENEFITS

This chemical process provides an attractive alternative with the following additional advantages:

a. Reduced Etchant Consumption

- Lower materials cost
- Lower overhead costs
- Reduced transportation and storage cost

b. Provides Improved Process Controls

- Improved yields
- Steady state processing
- Predictability

c. Reduced Potential Environmental Liability

- 92% Etchant recovery "in house"
- Copper metal recovery "in house"
- Effluent costs reduced by treating rinse waters

PROCESS DESCRIPTION

Basically the technology utilizes a solvent extraction, wherein the spent etching solution is intimately mixed with an organic reagent in a hydrocarbon base. This reagent material selectively extracts copper from spent etching solutions and transfers it through a series of mixing and selecting chambers to an acid media which is then circulated through an electrowinning cell where the copper is plated out in cathode form. Once the copper is removed the regeneration of etchant is performed by adding a small quantity of replenisher and ammonia. Refer to Figure 1.

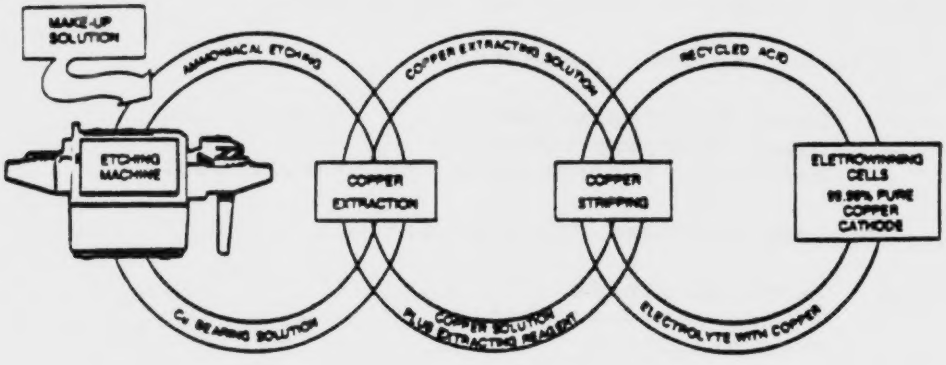
MAKE-UP SOLUTION
AMMONIACAL ETCHING
COPPER EXTRACTING SOLUTION
RECYCLED ACID
ETCHING MACHINE
COPPER EXTRACTION
COPPER STRIPPING
ELETROWINNING CELLS
99.98% PURE COPPER CATHODE
Cu BEARING SOLUTION
COPPER SOLUTION PLUS EXTRACTING REAGENT
ELECTROLYTE WITH COPPER

Figure 1. Mecer Process Overview

TECHNICIAL DESCRIPTION

The Mecer Process, as applied here, is based on a two unit operation: solvent extraction and electrowinning.

The first unit operation, refer to Figure 2, is the solvent extraction module, which is divided into three stages:

1. Extraction of copper from the spent etchant
2. Extraction of copper from the rinse water
3. Re-extraction of copper to a sulfuric acid solution

In the first extraction stage, see Table 1., spent etchant containing 18 oz/gal of copper is mixed with an organic solution containing an organic reagent in a mixer-settler tank. Some of the copper reacts with the organic reagent and forms a chemical complex which is more soluble in the organic phase than the etchant solution. This etching solution, with it's copper concentration, now reduced to 12 oz/gal copper is fed back into the process through an activated carbon filter. This solution, replenished with fresh replenisher equivalent to that lost due to evaporation and drag-out is now capable of etching an amount of copper corresponding to that extracted. The pH of this replenished etchant is automatically controlled by addition of aqueous ammonia.

In the second stage, copper is extracted from the rinse waters in an analogous fashion as in the first extraction stage. Rinse waters usually leave the extraction module with a concentration of less than 5 mg/l copper. One half of this rinse water is recirculated back into the process through carbon filtration, while the other half is sent to the final pH adjustment waste treatment system and then discarded into the sewage system.

In the third and final extraction stage the organic solution (from the two previous extractions) is mixed with a sulfuric acid solution. This metal organic complex is then split and the copper dissolved (extracted) into the sulfuric acid as an electrolyte, while the organic solution (with the reagent) is recycled for renewed extraction of copper.

The second unit of operation, as shown in Figure 2, is the electrowinning module, which produces electrolytic copper from the copper laden sulfuric acid solution.

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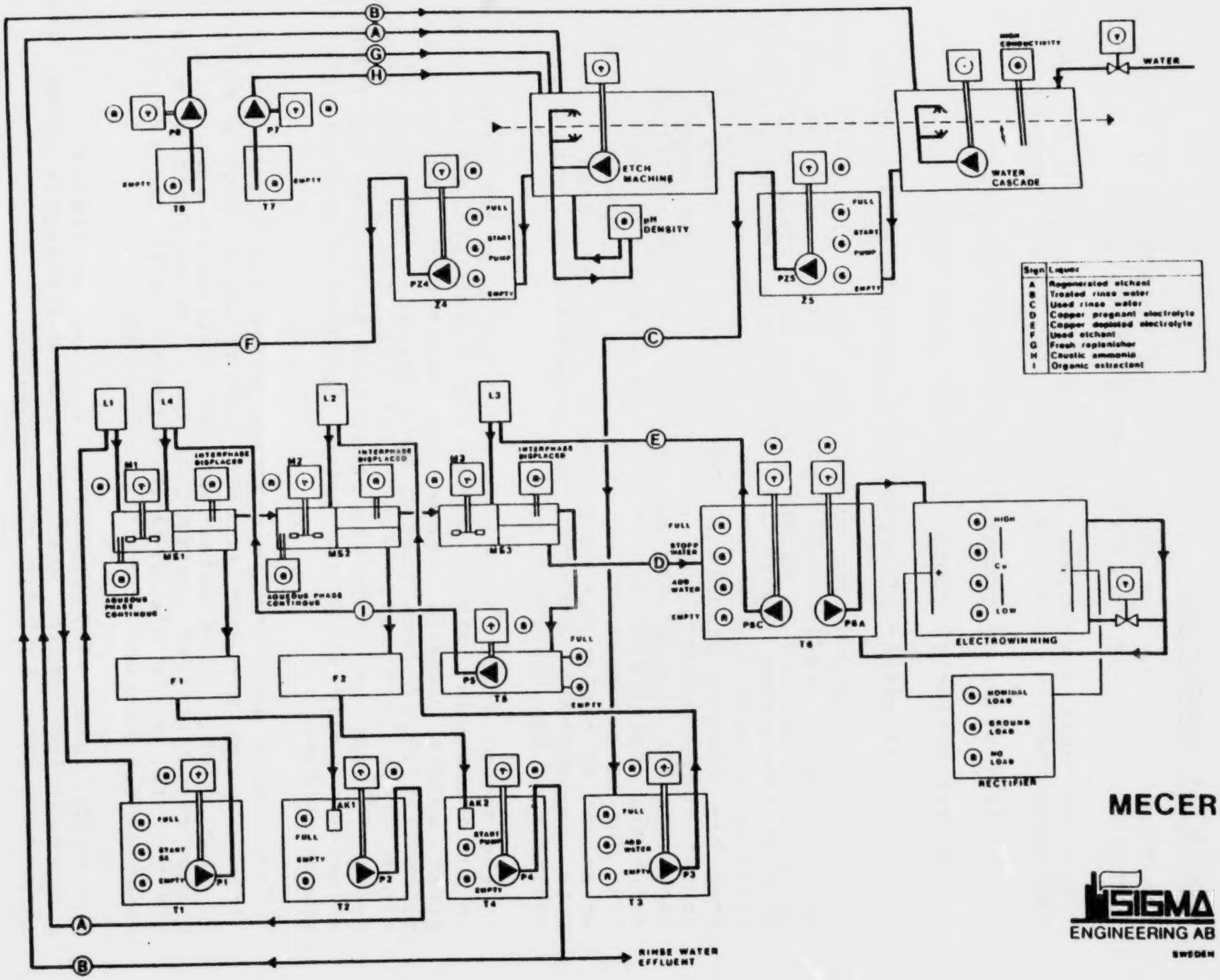
WATER
HIGH CONDUCTIVITY
WATER CASCADE
ETCH MACHINE
pH DENSITY
Z4
PZ4
Z5
PZ5
FULL
START PUMP
EMPTY
P8
P7
T8
T7
B
A
G
H
C
E
F
D
I
L1
L4
L2
L3
M1
M2
M3
MS1
MS2
MS3
INTERPHASE DISPLACED
AQUEOUS PHASE CONTINUOUS
F1
F2
T5
P5
T6
P6C
P6A
STOPP WATER
ADD WATER
ELECTROWINNING
HIGH
Cu
LOW
RECTIFIER
NOMINAL LOAD
GROUND LOAD
NO LOAD
T1
T2
T4
T3
P1
P2
P4
P3
AK1
AK2
START 66
RINSE WATER EFFLUENT
Sign Liquor
A Regenerated etchant
B Treated rinse water
C Used rinse water
D Copper pregnant electrolyte
E Copper depleted electrolyte
F Used etchant
G Fresh replenisher
H Caustic ammonia
I Organic extractant
MECER
SIGMA
ENGINEERING AB
SWEDEN

Figure 2. Mecer Process Flow Schematic

Table 1.

Chemical Expressions for Etching and Recovery Processes

Etching of Copper Metal from Printed-Wiring Boards (PWBs):

$$Cu^{o} + 2NH_3 + 2NH_4Cl + 1/2O_2 \longleftrightarrow Cu(NH_3)_4Cl_2 + H_2O$$

Extraction of copper from spent etchant:

$$Cu(NH_3)_4Cl_2 + 2RH_{\text{--org}} \longleftrightarrow CuR_{2\text{--org}} + 2NH_3 + 2NH_4Cl$$

Re-extraction of copper to the electrolyte:

$$CuR_{2\text{--org}} + H_2SO_4 \longleftrightarrow CuSO_4 + 2RH_{\text{--org}}$$

Electrowinning of copper metal from the electrolyte:

$$CuSO_4 + H_2O \longleftrightarrow Cu^{o} + H_2SO_4 + 1/2O_2$$

If the three last expressions are added together the resulting expression is:

$$Cu(NH_3)_4Cl_2 + H_2O \longleftrightarrow Cu^{o} + 2NH_3 + 2NH_4Cl + 1/2O_2$$

This expression is the reversed expression for etching (compare the first expression).

OPERATING EXPERIENCE

Since the startup of this unit in November, 1984 it has been running consistently without major downtime problems. The regenerated etchant solution, supplied to both the inner and outer layer etchers, has been performing above expectations without any adverse effects on product quality.

Only two minor changes were required in our etching equipment in order to accomodate this process. The first change involved the rinsing step prior to the etching chambers. Squeegee rollers had to be installed prior to the etching chamber to avoid excess drag-in of rinse waters. The second change involved the installation of squeegee rollers in the transition stage between the exit of the etching chamber and the rinse chamber. This drag-out was shown to be excessive and caused a higher than expected copper in the treated rinse waters.

The Mecer process has also proved to be compatible with our other manufacturing processes. For example, there has been no effect on fully aqueous dry film used in the inner layer fabrication process nor have any adverse effects been seen on the tin/lead resist in our outer layer processes. Also, solderability at reflow has been observed to be completely acceptable.

This process is designed to operate continuously with minimal human intervention. There are some labor intensive parts such as, the required preventive maintenance and unloading of plated cathodes every 600 hours. It has sensors which monitor the solution level in the tanks and a full alarm system in case of emergency (low and high level, current overload, interphase displacement, aqueous phase continuity, low and high copper concentration in the electrowinning cells).

The combined capacity of our unit is 60 tons per year copper with an actual electrowinning capacity of 21.2 lb/hour. The control of this chemical process as well as the etching system will be performed by means of a computer in the very near future.

SAVINGS

The initial return on investment (ROI) of this project, which included incremental operating unit costs, was a very attractive 52%. A recent review of the project shows the actual savings are very close to those projected.

For our facility, the savings were captured in three areas:

1. Reduction in chemical consumption.
2. Transportation cost avoidance (reduced shipment of spent etchant).
3. Income from copper sales.

Our experience to date has shown a reduction in chemical consumption of 85% to 90%, which corresponds to 53% of our savings. We are confident that these savings will increase even more as we fine tune the equipment and process so the makeup solution just balances the losses due to evaporation and drag-out. Process experience by others has shown a 95% reduction in fresh etchant usuage is attainable.

Income from copper sales has been less than projected due to lower market demand. However, the project produces net savings.

Besides the financial benefit, it is important to note that our exposure to environmental liability for spent etchant shipped has been drastically reduced since the unit was started.

SUMMARY

Based on our experience to date, the MECER PROCESS has been demonstrated to be reliable in regenerating etchant product that meets all our requirements in terms of chemical composition and consistency.

It should be pointed out, savings obtained with the implementation of the MECER PROCESS are instantaneous because a drop in the consumption of fresh replenisher is observed immediately.

ACKNOWLEDGEMENTS

The authors would like to thank Raphael Rodriques-Diaz from Digital Equipment Corporation in San German, Puerto Rico and David Lipka from Digital Equipment Corporation in Andover, MA for their significant contributions that helped make this program a success.

ABOUT THE AUTHORS

Carlos Rivera is a Chemical Process Engineer at Digital's Printed- Wiring Board facility, in San German, Puerto Rico.

Gary DeClue is a Process Engineering Manager at Digital's Technology Center, in Andover, MA.

THE USE OF RECYCLING AS A MEANS TO COMPLY WITH RCRA AND TO LOWER THE COST OF WASTE TREATMENT

by Phil Edelstein, Manager, ERS Div.
CP Chemicals, Inc.

INTRODUCTION

Metallic chemical recycling is an effective means of complying with RCRA. The chemical and metals reclaiming industry is going through rapid changes and expansion to fill a new need in the plating and printed circuit marketplace.

With the enforcement of the Clean Water Act and RCRA, solid waste disposal has increased dramatically since the 1970's. New provisions in RCRA 1984 call for eliminating all hazardous waste from landfills by 1987 or 1988. Most of the solid and liquid waste generated by platers and PC shops is classified as hazardous waste in part due to the presence of heavy metals.

Many waste materials containing metals, inorganic and organic chemicals that presently end up in landfills will be recycled in the future, eliminating environmental liability and lowering costs.

This will be accomplished by the recycling and reclaiming industry developing technology to re-use waste materials that were of no interest in the past. At the same time platers and PC shops along with their suppliers will alter plating, etching, stripping and other processes so that a recycleable waste results without a loss of plating quality.

The other change will be in the operation of waste water treatment plants in PC and plating shops.

A platers waste water treatment plant is a "miniature" chemical plant. The same equipment and chemical engineering technology are used by platers in waste treatment and by metallic chemical recyclers in chemical manufacturing.

Waste water treatment sludges, as well as old plating baths, various etchants and strippers are crude raw materials for recycling plants. As landfill space declines and disposal costs rise chemical recycling and reclaiming are easy routes to low cost compliance with RCRA.

There are two basic sources of waste in a PC or plating shop. Spent process solutions such as etchants, plating baths, strippers, pickle acids and cleaners. Spent etchants and strippers contain the most metal, up to 10% by weight. Plating baths are 2 - 5% metal. Cleaners and pickle acids are often lowest in metal content. However, all these waste materials have a higher metals concentration than rinse water which is generally 30-150 ppm.

The spent process solutions with metals content of over 2% are directly recycleable. The plater can ship these wastes to a recycling plant without any treatment.

Spent cupric chloride etchant from the PC industry is a prime example. This material contains up to 10% copper (as metal) and 20% free hydrochloric acid. The recycler gets copper and an oxidizer (the hydrochloric acid), both of which are used to make various copper chemicals. In some cases the generator of waste cupric chloride etchant has a net dollar gain from the recycling of this material.

Economics and chemistry are at work in this example of recycling. The cost to recycle waste cupric chloride etchant into other copper chemicals is much lower than the cost to waste treat and dispose of the resulting sludge.

Many PC shops and platers slowly bleed concentrated process solutions into their waste treatment systems. This is done because most treatment systems are designed to deal with the metals concentration of rinse water. Highly concentrated solutions overload the system and result in out-of-spec effluent.

Some PC shops batch treat concentrated solutions. If metals segregation is maintained the resulting sludge is often recycleable. However, the batch treatment technique can be the same process as used by a chemical recycler, and may be unnecessary for the waste generator. For example, the sludge made from spent cupric chloride etchant would have to be re-dissolved in acid by the recycler before it can be processed as a raw material.

Platers and PC shops may be able to avoid the cost of batch treatment altogether by having an outside recycler take the untreated spent solution. The recycler can take advantage of economies of scale and process these solutios at a much lower cost. The metal contained is applied as a credit towards the processing cost because the metal becomes another useful metallic chemical for sale.

Rinse water requires treatment by the plater or PC shop to concentrate the metals contained. Various methods can be used to concentrate rinse water for recycling. Chemical precipitation is the most common method. Evaporation, electrodialysis, reverse osmosis and ion-exchange can also be used to concentrate rinse water but at a higher cost than precipitation.

In the use of all these technologies metal segregation is the key. In several PC plants ion-exchange is used for the chelated rinses and the ion-exchange discharge is then precipitated along with the non-chelated rinses. If practical the ion-exchange discharge can be sent to a recycler directly, avoiding the cost of precipitation, if the solution is concentrated enough.

Most PC plants and platers usually have one metal that is up to 50% or more of the total metal in their effluent. To help fulfill the "waste minimization" clause in RCRA 1984 this primary metal should be recycled first. For PC plants this primary metal is copper, accounting for 70 - 90% of total metal in a PC shops effluent.

A job-plater in the Northeast provides 40 different finishes to their customers, yet nickel is 60% of the total metal in the waste treatment material.

In some plants recycling methods can be employed to return rinse water to the plating tank. However, in some instances platers can recycle useing an outside chemical reclaimer at the same or lower cost (per pound of metallic salt) than in-house drag-out recycling. Platers can "exchange" their waste metallic chemicals for virgin salts based on a pound for pound convertion formula. This recycling option has several benefits which include allowing the plater to make bath additions with pure metallic salts rather than with reclaimed material.

Recyclers accomplish this metals exchange by using the platers "metal" to make products for non-electroplating applications, where high purity chemical specifications are not required. The plater then receives metallic salts made from pure or virgin metal, to complete the exchange.

All wet processes in the plating shop and all waste treatment procedures should be analyzed from the standpoint of chemical through-put rather than plating through-put, when looking for recycling opportunities. For example, when stripping nickel-chrome plated parts or racks, the chrome should be removed in caustic first and the nickel removed in acid second. This creates two waste solutions instead of one, but both are recycleable, especially the nickel in acid. Strip solutions should be used as long as possible and practical, because the more metal contained per volume of waste stripper the better the recycling economics. The freight cost per pound of metal is reduced and the recyclers efficiency is improved.

The same is true for etchants in the PC industry. Ammonium and sodium persulfate etchants often still have etching capacity when they are dumped. Also methods are being developed to lengthen the life of these solutions thereby increasing the amount of dissolved copper. This lowers waste volume and increases recycle potential.

Specific precipitation methods can increase recycle potential substantially for waste water treatment sludges.

A PC shop had been precipitating copper with lime (to raise the pH) and ferrous sulfate (as a flocculent). This PC shop switched to caustic soda and an anionic flocculent. As a result the PC shop cut the sludge volume to one third of previous production. This had the effect of increasing the copper content by three-fold. Effluent standards are maintained while a recycleable copper raw material is produced, instead of sludge for the landfill.

There are several advantages at work here. The addition of ferrous sulfate is an impurity in copper recovery. The anionic flocculent can be filtered out or burned in the recovery process. The sodium in caustic soda can be removed easily in the reclaimers process. The calcium in lime is harder to remove in the reclaiming process.

Other volume reduction techniques can be employed to aid recycling. These techniques lower freight costs to the reclaimers plant and can increase the reclaimers efficiency. However, since sludge driers and evaporators are very energy intensive the cost effectiveness of this equipment must be evaluated carefully. The reclaimers may be able to offer the plater a cost value comparison for the use of a sludge drier or evaporator.

CONCLUSION

The shortest, least costly and least complicated method of recycling waste metallic chemicals generated by plating and PC manufacturing operations is to have these wastes recycled into other chemicals, by large-scale chemical recovery plants.

As platers change their operations to generate more recycleable wastes, chemical reclaimers will look for new products that can be made from these waste raw materials.

The economics of this kind of recycling will vary with distance to a reclaimer, the quality and quantity of waste generated, the value of recovered chemicals and metals, the cost of available landfill space and political considerations that may affect the world supply of virgin metals and chemicals.

Driven by RCRA 1984 and the environmental liability of landfilling hazardous waste, metallic chemical recycling is a viable technology for maintaining EPA compliance in plating and PC shops.

EVALUATION OF OPERATION AND MAINTENANCE MODIFICATIONS TO REDUCE TTO FROM METAL FINISHING OPERATIONS

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Introduction

The United States Environmental Protection Agency (EPA) has promulgated regulations to control the discharge of Total Toxic Organics (TTO) from metal finishing processes. These regulations set the maximum concentration of TTO in discharge waters at 2.13 mg/L as a maximum concentration for any one day in the process streams. The regulations are defined and TTO compounds are listed in 40 CFR 433 subpart A. The U.S. Army Toxic and Hazardous Materials Agency (USATHAMA), in response to these and other environmental regulations, increased its efforts to identify, quantitate, and mitigate Army generation of hazardous materials. As part of this effort, USATHAMA sponsored several projects through EPA. The topic of this paper is the results from one of those projects.

The U.S. Army operates extensive metal finishing processes at its various maintenance depots. The depots are receiving increased pressure to control and reduce toxic and hazardous waste discharges. The goal of this project was to identify simple and inexpensive maintenance and operational changes in metal finishing processes that would reduce TTO discharges. The project was carried out in four phases. The first phase involved identifying depots and process lines amenable to quantitation of their discharges, performing preliminary surveys of the lines, and selecting two depots for further study. The metal finishing and associated processes at the selected facilities were then tested for one to two weeks. From the results of these tests, recommendations were drawn up and, where the sites concurred, implemented. Finally, the sites were retested to determine if TTO discharges had been reduced.

Conclusions

The study was successful in identifying operation and maintenance modifications that reduced TTO discharges at the affected facilities. The major conclusions reached in this study deal with the paint stripping operations using TTO based stripping solvents (e.g., MS-111). It was found that this operation contributed the vast majority of the measured TTO being discharged by the metal finishing facilities studied. Specifically, overflow from the paint stripper rinse tanks discharging methylene chloride and phenol to the drains was the primary source of TTO. In each case, by isolating the first rinse tank from direct discharge to the sewer system, TTO was reduced by factors of 4 or more.

Site Descriptions and Recommendations

The metal finishing facilities at the Sacramento (California) Army Depot and the Tobyhanna (Pennsylvania) Army Depot were selected for study in this program. A site survey of the Sacramento facility was conducted in June 1984. The preliminary testing was conducted in August 1984 and the final testing was conducted in October 1985. The site survey at the Tobyhanna facility was conducted in November 1984, the preliminary tests were carried out in January 1985, and the final tests were performed in September 1985. A list of the major TTO compounds detected at the two facilities is given in Table 1. Major non-TTO compounds identified in the process streams under study is given in Table 2. After the initial tests were conducted, both general and specific recommendations were given to each facility. The general recommendations included the usual admonitions about good housekeeping and the isolation of solvent handling areas from sewer drains. The specific recommendations applicable to the individual facilities are presented below.

The primary mission of the Sacramento Army Depot is the repair of electronic equipment. The plating shop averages 15,000 to 20,000 "pieces" per week throughput. Depot discharges are segregated with the plating shop and graphic arts facility discharges going to a pretreatment plant onsite. Discharge from the pretreatment plant is to the county Publicly Owned Treatment Works (POTW). Other discharges from the depot go directly to the sanitary sewer. Waste water from the pretreatment plant averages 24,000 to 32,000 gpd with about 98 percent coming from the plating shop. A diagram of the flows at Sacramento is given in Figure 1.

Two primary recommendations with respect to the paint stripping operation were presented to the Sacramento Army Depot staff. The first recommendation was an operational change, suggesting a rerouting of the flow of material. Initially, material was removed from the MS-111 stripper tank and rinsed in a flowing cold water rinse tank. The material was then transferred to a hot caustic stripper tank and finally returned to the cold water rinse tank (Figure 2a). It was recommended that the first rinse be abandoned, that the material be taken directly from the MS-111 tank to the hot caustic tank. The second recommendation represented a hardware change. It was suggested that the overflow line from the cold rinse tank be plumbed as the make-up line to the hot caustic tank rather than discharging directly to the acid/caustic drain (DAC) line. These recommendations are shown in Figure 2b.

The mission of the Tobyhanna Army Depot is similar to that of the Sacramento Depot, that is, the repair and maintenance of electronic hardware. The plating shop averages about 500 "jobs" per week. Because the number and size of "pieces" per "job" varied so widely, it is difficult to compare on a one-to-one basis the two facilities (Tobyhanna and Sacramento. However, by observation it appeared that the Tobyhanna plating shop had a higher rate of throughput than the Sacramento shop. Depot discharges are segregated, with the plating shop discharges going to a pretreatment plant. All other discharges go to a tertiary treatment plant onsite. The expected sources of TTO and the flow path of their discharges is shown in Figure 3. The dotted lines show suspected but unconfirmed floor drains from the printed circuit room and the photo lab to the main sewer bypassing the photo room sump. The tertiary treatment plant treats from 2 million to 2.5 million gallons per week. This plant operates 24-hours per day 7 days a week. The plating shop treatment plant operates approximately 10 hours per day (more if two shifts are working in the shop and 5 to 6 days a week. Its throughput is approximately 18,000 gpd or 110,000 gallons per week. The plant also generates about 3 drums of hazardous waste a month.

The major recommendation presented by the project and acted on by the site concerned a plumbing change at the paint stripper rinse tank. Initially it was plumbed as a flowing rinse tank. It was recommended that the tank be replumbed to a still rinse for the first tank and a flowing rinse for the second tank (see Figure 4).

Results and Discussion

The results of sampling and analysis at the Sacramento Army Depot are presented in Tables 3 and 4, and the results for the Tobyhanna tests are given in Tables 5 and 6. Tables 3 and 5 list the sampling locations, the estimated flowrates during the sampling periods, and the concentrations observed. The flowrates are mostly observed values, but some are engineering estimates. The TTO values are the averages of the sums of identified and quantitated TTO compound concentrations observed in the respective streams. That is, the concentrations of individual TTO compounds measured in a given sample are summed. All samples from an individual stream are then averaged. The non-TTO compounds are handled in the same manner. The TOC values are the average of all values for a particular stream. Tables 4 and 6 present the total mass discharge per week of each pollutant category for each stream during the corresponding test periods. These values are calculated from the concentrations and flowrates and are normalized to a 48-hour production week. The actual work weeks varied from 40 hours to 78 hours.

Volume flow values at the Sacramento facility did not appear to change significantly between the two sampling periods (see Table 3). However, the implementation of the recommendations concerning the paint stripper rinse tank appears to have reduced the concentration of TTO by a factor of seven. While the original concentration of TTO in the DAC line (the line collecting over-flow from the rinse tank) would be out of compliance (5.0 versus 2.13 mg/L) if it were a discharge stream, the concentration after implementation is well within compliance (0.7 mg/L). The reduction in total TTO discharge is presented very clearly in Table 4. An interesting observation in Table 4 is the decrease in TTO as the material moves from the DAC line through the Combined Effluent Sump to the Equalization basin. This is probably caused by vaporization of volatile TTO (methylene chloride). The mass of methylene chloride (the major TTO compound in these streams) is seen to decrease as it passes through the system.

Non-TTO compounds seen at Sacramento were primarily paint solvents and came from the graphic arts area. This can be seen in both the high concentration (Table 3) and in the high weekly mass flowrate (Table 4) during the first testing period. Housekeeping recommendations concerning the isolation of solvents from floor drain areas resulted in the dramatic decrease in these pollutants. Non-TTO compounds are listed and discussed because they may become controlled. They also may be precursors of TTO compounds in the system. For example, significant levels of isophorone (a TTO compound) was seen in all the graphic arts samples, yet no source could be identified. Isophorone can be generated from acetone under caustic conditions. Acetone was a major non-TTO compound seen in the graphic arts discharge.

Essentially the same results as seen at Sacramento were observed at Tobyhanna. That is, the paint stripper rinse tank plumbing changes apparently reduced the TTO levels by a factor of 6 (from 182 to 27 mg/L) in the effluent directly from the rinse tank and by a factor of 4 (9.2 to 2.0 mg/L) in the A/A sump. The reason for the sharp reduction in TTO between the A/A sump and the treatment plant discharge during the second sampling period is not known, but it is postulated that both volatilization of volatile TTO and chemical reaction of nonvolatile TTO may have occurred during the treatment process. Both methylene chloride and phenol, the two major TTO components coming from the plating shop, were markedly reduced. These compounds are major constituents of MS-111 and other paint stripping solvents. Another indication that the plumbing change was decreasing TTO and non-TTO in the plating shop effluent was the increase in waste removed from the still rinse tank from about one barrel every month to one barrel every two weeks. No change was seen in the paint spray booth discharge and none was expected. The site did not implement the recommendations for this source.

Sampling and Analysis Methods

Sampling and analysis methods used in this study are standard procedures. Modifications have been made only when required to obtain the sample. Three types of samples were generated from each stream, a volatile organic analysis (VOA) sample, a base-neutral/acid analysis (BNA) sample, and a total organic carbon analysis (TOC) sample. The BNA and TOC samples were taken from a daily composite sample collected with an ISCO composite sampler at each flowing stream location. The samplers were adjusted to collect a fixed volume (approximately 100 mL) every 5 minutes. At certain Tobyhanna locations (the paint spray booth reservoir, the sonic baths, and the sulfide plant effluent) 1-gallon grab samples were obtained. VOA samples were obtained by hand once every hour during the compositing period. TOC samples were preserved with sulfuric acid to pH <2 for shipment. Samples were shipped to the laboratory on ice by overnight air express. The VOA samples were composited in the laboratory for analysis.

Analysis was by standard EPA methods. VOA analysis was by EPA Method 624 using gas chromatography/mass spectrometry (GC/MS). BNA analysis was by Method 625, also using GC/MS. These methods are defined in Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, EPA-600/4-82-057, July 1982. Total Organic Carbon (TOC) was determined by EPA Method 415.1 from Methods for Chemical Analysis of Water and Waste, EPA-600/4-79-020, March 1979.

Acknowledgements

This project was funded by the USATHAMA and was conducted by the USEPA Water Engineering Research Laboratory in Cincinatti, Ohio. The material presented here does not necessarily represent the position or policy of either agency. This project could not have been carried to a successful conclusion without the active support of staff at both Army depots. Of specific and invaluable assistance were the treatment plant staff at Sacramento and the plating shop foremen and staff at Tobyhanna. In addition were the environmental officers, Mr. Pat Christman at Sacramento and Dr. Mary Daly at Tobyhanna, and their respective staffs.

List of Figures

Figure 1. Schematic of the process stream flows at the Sacramento Army Depot.

Figure 2. Schematic of the process changes around the paint stripper rinse tank recommended for the Sacramento Army Depot.

Figure 3. Schematic of the process stream flows at the Tobyhanna Army Depot.

Figure 4. Schematic of the process changes around the paint stripper rinse tank recommended for the Tobyhanna Army Depot.

Table 1. Partial list of TTO compounds including those detected at the Sacramento and Tobyhanna Army Depots.

Benzene
Bis(2-chloroethyl)ether
Bromomethane
Carbon tetrachloride
Chloroethane
Chloroform
Chlorobenzene
Chloromethane
2-chlorophenol
1,3-dichlorobenzene
1,2(t)-dichloroethane
1,1-dichloroethane
1,1-dichloroethene
2,4-dichlorophenol
2,4-dimethylphenol
4,6-dinitro-2-methylphenol
2,4-dinitrophenol
Ethyl benzene
Fluorene
Isophorone
Methylene chloride
Naphthalene
2-nitrophenol
4-nitrophenol
N-nitrosodimethylamine
p-chloro-m-cresol
Pentachlorophenol
Phenanthrene
Phenol
1,1,2,2-tetrachloroethane
Tetrachloroethene
1,1,1-trichloroethane
Trichloroethene
2,4,6-trichlorophenol
Toluene

Table 2. List of major non-TTO compounds identified at Sacramento and Tobyhanna Army Depots.

Acetone
Aniline
2-Hexanone
Methyl ethyl ketone
2-methylnaphthalene
2-methylphenol
Xylenes
4-methyl-2-pentanone
Styrene
4-methylphenol
benzoic acid
Dibenzofuran
2-nitroanaline

Table 3. Volume flowrates and concentrations of TTO and non-TTO compounds and TOC at Sacramento Army Depot.

Sample Site	Wastewater Flow (L/min)		TTO Concentrations (mg/L)		Non-TTO Concentrations (mg/L)		TOC Concentrations (mg/L)	
	8/84	10/85	8/84	10/85	8/84	10/84	8/84	10/85
DAC	112 ± 15	115 ± 15	5.2 ± 1.4[a]	0.7 ± 0.4[b]	0.01 ± 0.01	0.01 ± 0.0	9 ± 3	10 ± 10
Graphic arts	0.5 ± 0.3	0.3 ± 0.2	0.23 ± 0.12	0.12 ± 0.09	60 ± 40	0.4 ± 0.3	100 ± 60	43 ± 17
Combined effluents	170 ± 25	140 ± 20	2.0 ± 0.9[a]	0.5 ± 0.3[b]	3 ± 2	0.2 ± 0.2	18 ± 5	10 ± 3
Equilization basin	200 ± 70	--	1.0 ± 0.5[a]	--	0.54 ± 0.04	--	19 ± 1	--

[a] Primarily methylene chloride and phenol
[b] Primarily phenol

Table 4. Mass flowrates (normalized to 48 hours) of TTO and non-TTO compounds and TOC at the Sacramento Army Depot.

Sample Site	TTO Concentrations (kg/wk)		Non-TTO Concentrations (g/wk)		TOC Concentrations (kg/wk)	
	8/84	10/85	8/84	10/84	8/84	10/85
DAC	1.7 ± 0.5	0.2 ± 0.1	3 ± 3	4 ± 4	2.9 ± 1.0	4.0 ± 2.7
Graphic arts	0.0003 ± 0.0002	0.0001 ± 0.0001	90 ± 80	0.3 ± 0.3	0.2 ± 0.1	0.04 ± 0.03
Combined effluents	1.0 ± 0.5	0.2 ± 0.1	2000 ± 1000	70 ± 70	8.6 ± 2.7	4.0 ± 1.3
Equilization basin	0.6 ± 0.3	--	310 ± 80	--	10.9 ± 2.8	--

M9

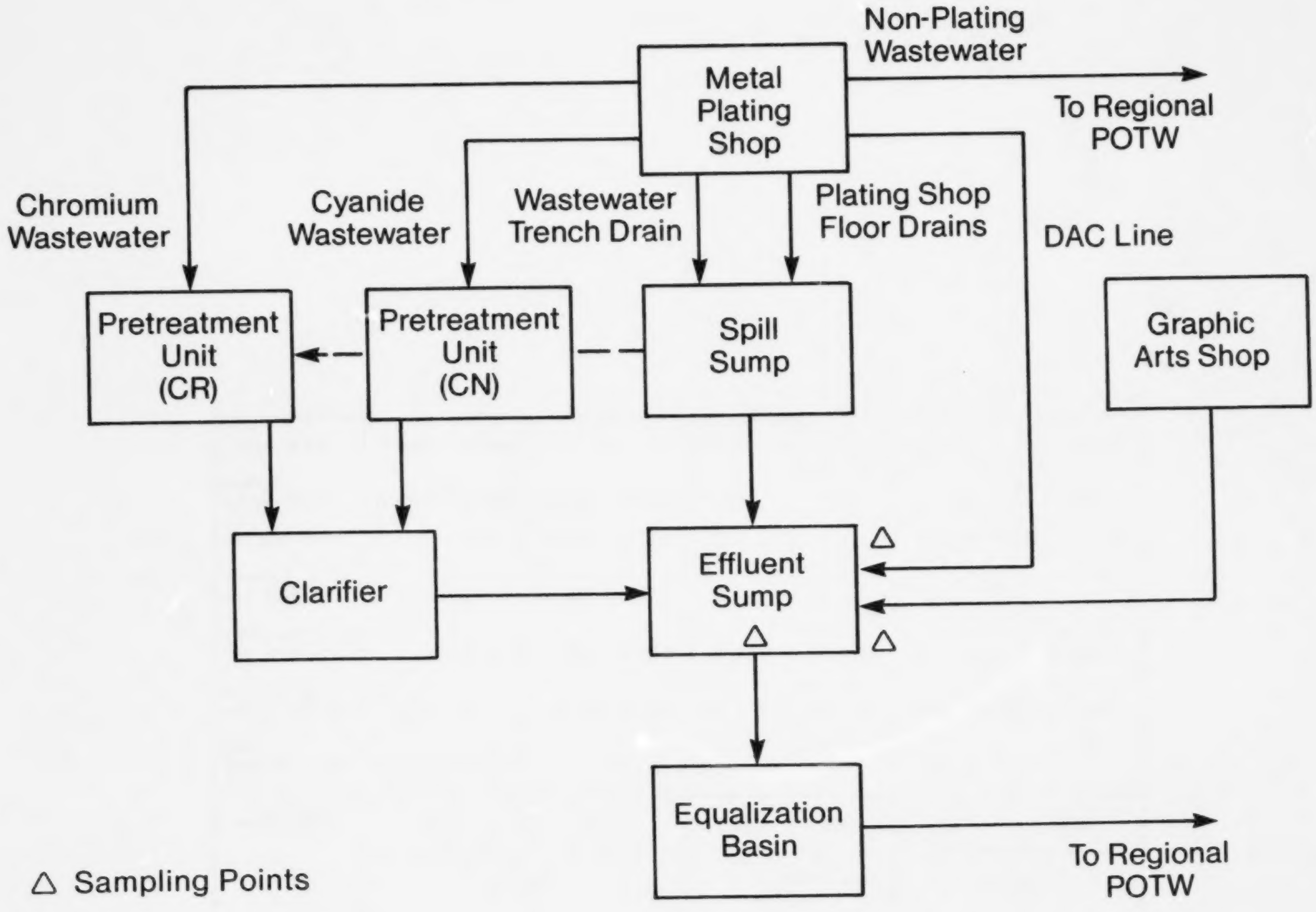
Table 5. Volume flowrates and concentrations of TTO and non-TTO compounds and TOC at Tobyhanna Army Depot.

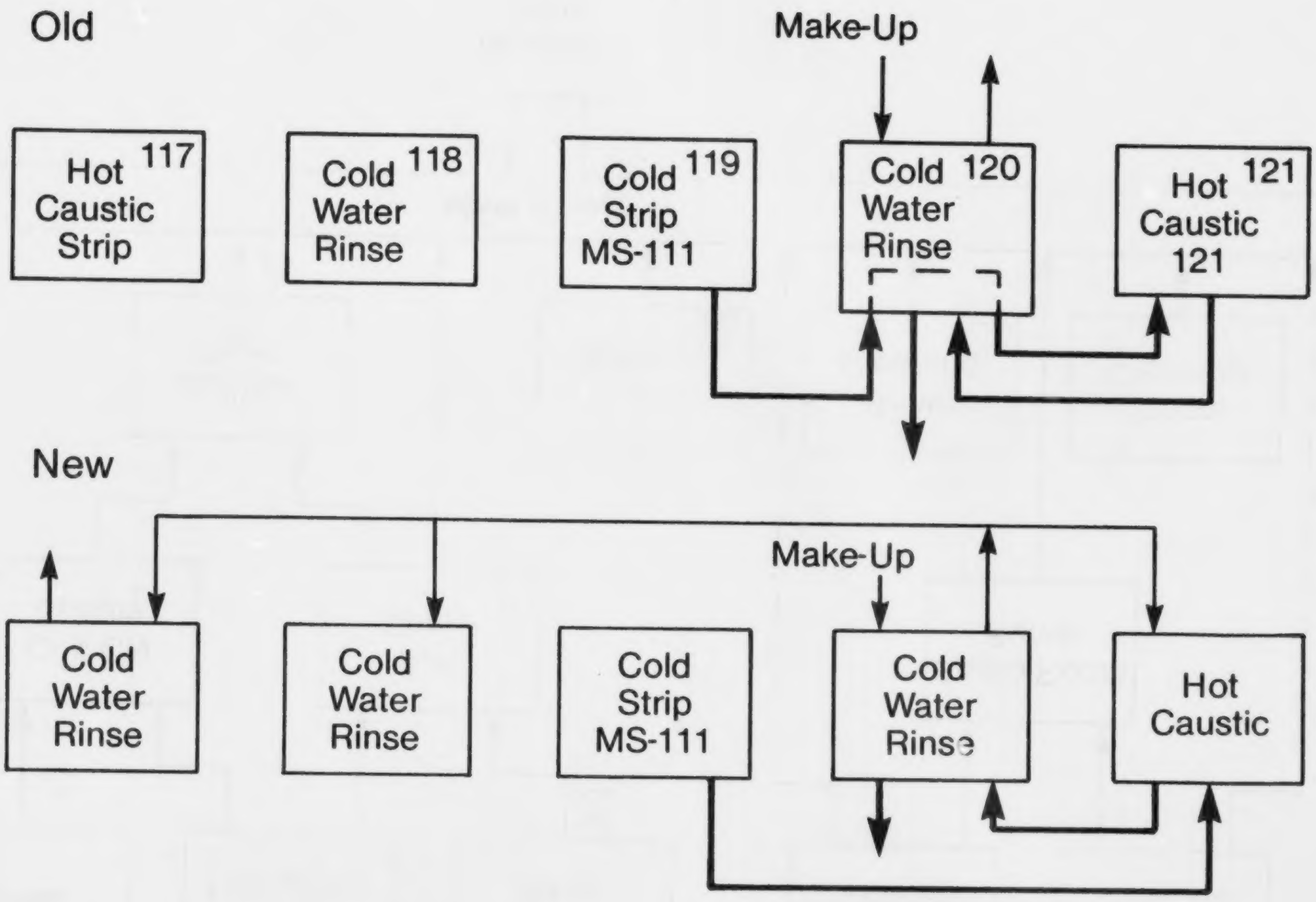
Sample Site	Measured Flow (L/min)		TTO Concentrations (mg/L)		Non-TTO Concentrations (mg/L)		TCO Concentrations (mg/L)	
	1/85	9/85	1/85	9/85	1/85	9/85	1/85	9/85
Cadmium rinse tank	4.8 ± 0.1	--	0.04 ± 0.03	--	0.04 ± 0.02	--	<5	--
Paint stripper rinse tank	4.1 ± 0.3	5.8 ± 2.5	182 ± 0.01	27 ± 18	0.61 ± 0.01	6.0 ± 0.7	350 ± 14	44 ± 9
A/A sump (sulfide)	109 ± 1	86 ± 9	9.6 ± 0.2	2.1 ± 1.0	0.22 ± 0.02	0.32 ± 0.08	14 ± 1	9.0 ± 0.8
A/A sump (sewer)	9.4 ± 3.0	0.5 ± 0.4						
Sulfide plant	135 ± 10	125 ± 10	8.04 ± 0.01	0.02 ± 0.01	0.08 ± 0.01	0.03 ± 0.01	13	4.1
Paint spray booths	5500[a]	5500[a]	1.3 ± 0.01	1.02 ± 0.01	7.4 ± 0.01	9.5 ± 0.01	680	1200
Sonic baths	2440[a]	--	3.3 ± 0.4	--	0.82 ± 0.23	--	460,73,30[b]	--

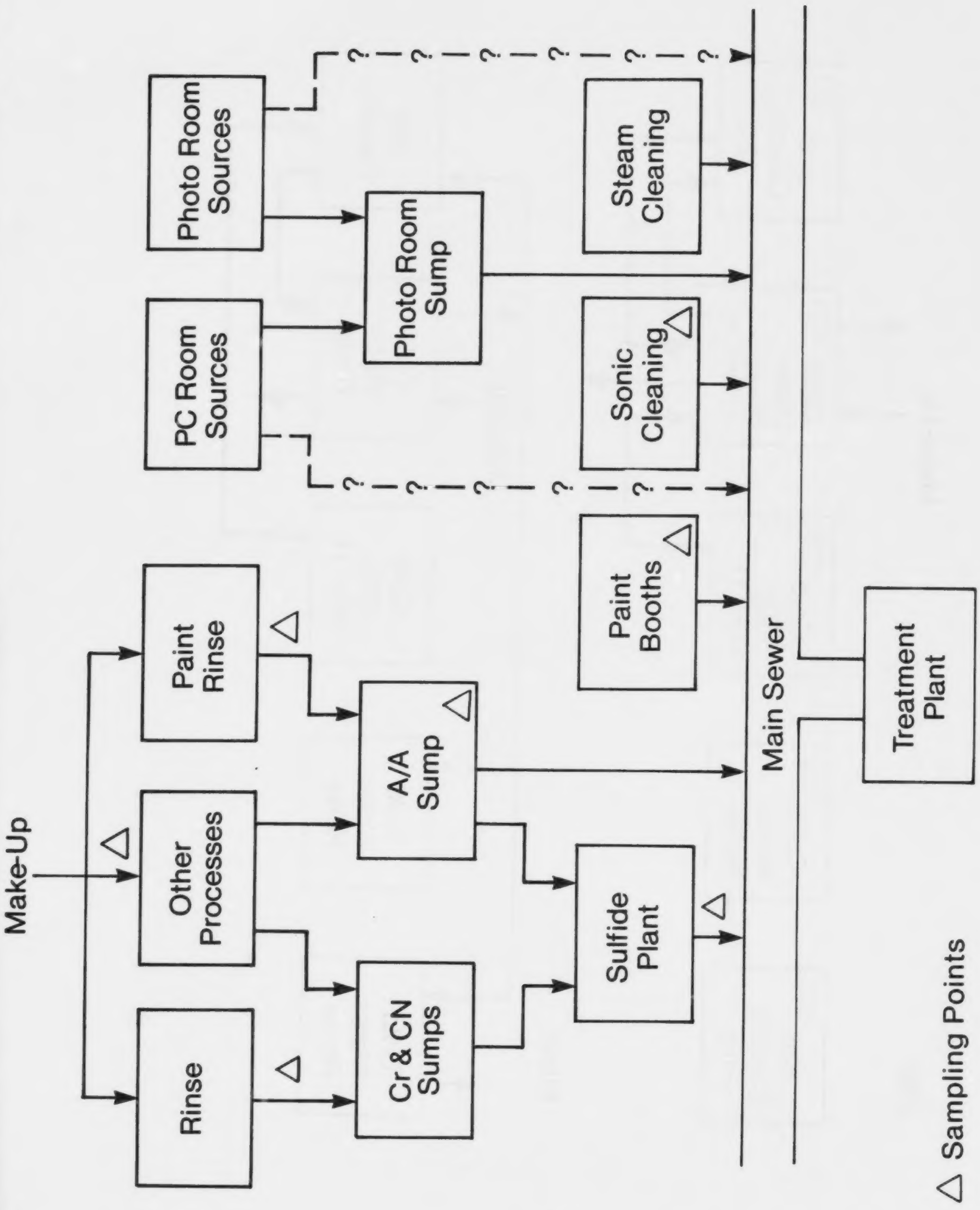
[a] Liters/week
[b] Three tanks

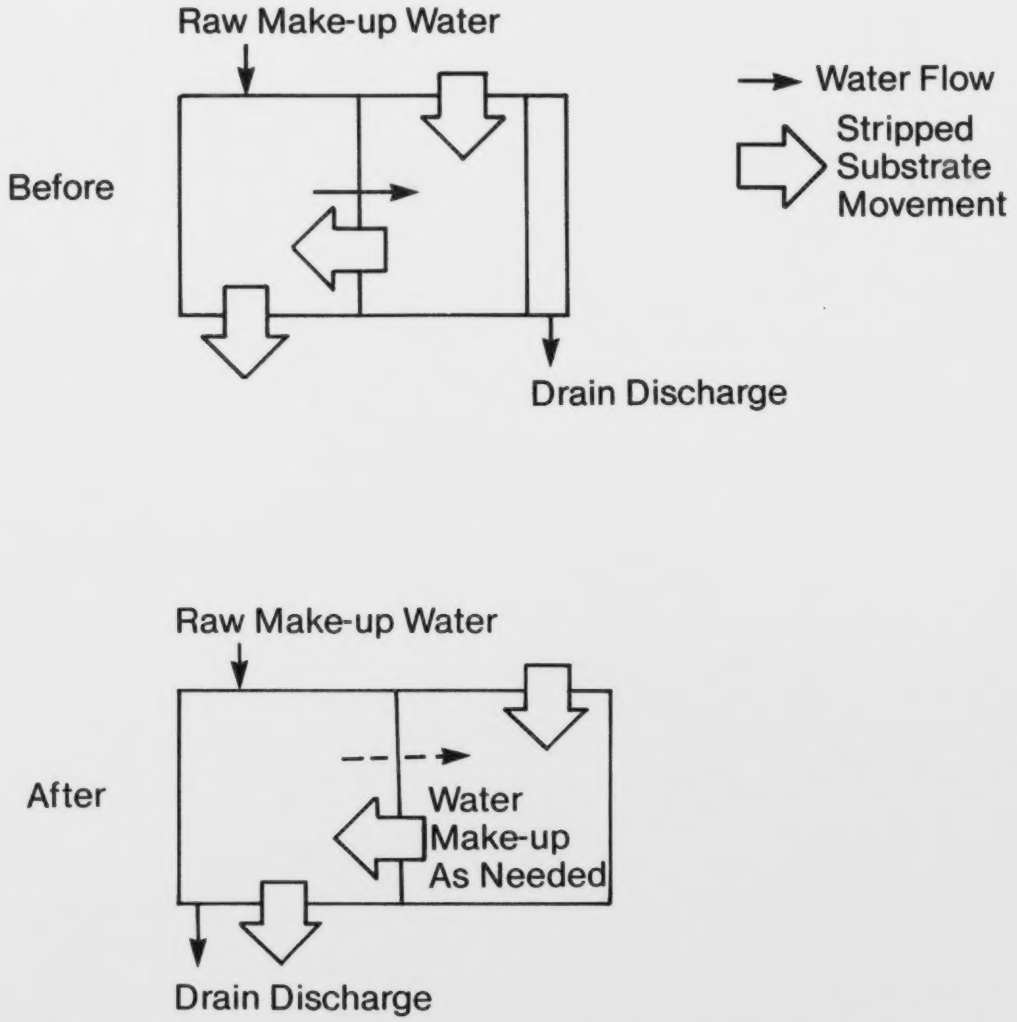
Table 6. Mass flowrates (normalized to 48 hours) of TTO and non-TTO compounds and TOC at the Tobyhanna Army Depot.

Sample Site	TTO (kg/wk)		Non-TTO (g/wk)		TOC (kg/wk)	
	1/85	9/85	1/85	9/85	1/85	9/85
Cadmium rinse tank	0.0005 ± 0.0004	--	0.5 ± 0.3	--	<0.07	--
Paint stripper rinse tank	2.2 ± 0.2	0.46 ± 0.30	6.9 ± 0.4	100 ± 40	4.1 ± 0.3	0.7 ± 0.4
A/A sump (sulfide)	2.99 ± 0.05	0.68 ± 0.39	69 ± 7	100 ± 20	4.4 ± 0.3	2.9 ± 0.2
A/A sump (sewer)	0.26 ± 0.09	0.003 ± 0.003	6 ± 2	0.5 ± 0.4	0.38 ± 0.12	0.02 ± 0.01
Sulfide plant	2.79 ± 0.01	0.006 ± 0.002	27 ± 3	9 ± 2	4.5 ± 0.04	1.1 ± 0.03
Paint spray booths	0.0049 ± 0.0001	0.0040 ± 0.0001	35	37	3.2	4.7
Sonic baths	0.0069 ± 0.0009	--	1.7 ± 0.5	--	0.5	--


Metal Plating Shop
Non-Plating Wastewater
To Regional POTW
Chromium Wastewater
Cyanide Wastewater
Wastewater Trench Drain
Plating Shop Floor Drains
DAC Line
Pretreatment Unit (CR)
Pretreatment Unit (CN)
Spill Sump
Graphic Arts Shop
Clarifier
Effluent Sump
Equalization Basin
To Regional POTW
△ Sampling Points


Old
Make-Up
Hot Caustic Strip 117
Cold Water Rinse 118
Cold Strip MS-111 119
Cold Water Rinse 120
Hot Caustic 121 121
New
Make-Up
Cold Water Rinse
Cold Water Rinse
Cold Strip MS-111
Cold Water Rinse
Hot Caustic


Make-Up
Rinse
Other Processes
Paint Rinse
Cr & CN Sumps
A/A Sump
Sulfide Plant
Paint Booths
PC Room Sources
Photo Room Sump
Photo Room Sources
Sonic Cleaning
Steam Cleaning
? ? ? ? ? ?
Main Sewer
Treatment Plant
△ Sampling Points


Before
Raw Make-up Water
Drain Discharge
Water Flow
Stripped Substrate Movement
After
Raw Make-up Water
Water Make-up As Needed
Drain Discharge

A CASE STUDY OF A MECHANICAL DRYER FOR METAL HYDROXIDE SLUDGE

at

STANADYNE, INC., SANFORD, NORTH CAROLINA

by George McRae, C.E.F.

The Stanadyne plant in Sanford, North Carolina, began drying metal hydroxide sludge with a mechanical sludge dryer[1] on September 17, 1985. The results achieved during the first four months of operation were as summarized in Table I.

TABLE I

OPERATING RESULTS

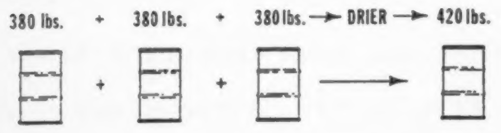
- Investment Payback: 1.49 YEARS
- Sludge Volume Reduction: 67% (3:1) (Figure 10, Table VII)
- Sludge Weight Reduction: 63%
- Increase in Sludge Stability
- Compliance with Waste Minimization Requirement

Figure 10

VOLUME AND WEIGHT REDUCTION —— SLUDGE REDUCER

AVERAGE WEIGHT FOR SLUDGE FROM FILTER PRESS = 380 lbs./DRUM

AVERAGE WEIGHT OF DRIED SLUDGE = 420 lbs./DRUM



1140 lbs. → 420 lbs. A 63.2% REDUCTION IN WEIGHT

3 → 1 A 66.7% REDUCTION IN VOLUM

---

[1] J-Mate™ manufactured by JWI, Inc.

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TABLE VII

STANADYNE VOLUME REDUCTION WITH DRIER

LBS		LBS/BARREL		# of BARRELS		DRIER		# BARRELS OF DRIED SLUDGE
600,000	÷	385	=	1560	÷	3	=	520
500,000	÷	385	=	1300	÷	3	=	433
400,000	÷	385	=	1039	÷	3	=	346
300,000	÷	385	=	779	÷	3	=	260
200,000	÷	385	=	520	÷	3	=	174
100,000	÷	385	=	260	÷	3	=	87
50,000	÷	385	=	130	÷	3	=	44

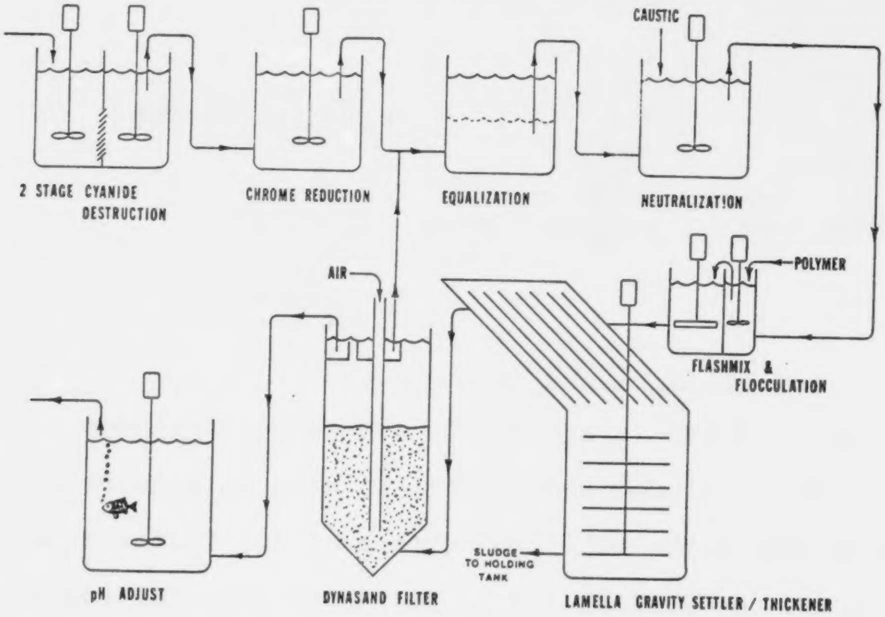
Background

The Sanford Plant of Stanadyne is a manufacturer of plumbing products, specifically the Moen faucet. In the production process, hazardous wastes are generated in the degreasing of brass fittings and, as a result, of the metal finishing operations including brazing, brite dipping, plating and stripping. The concept of "making pollution prevention pay" through in-process waste reduction has been applied in a comprehensive approach that has achieved savings of raw materials and reduced the load on the wastewater treatment system.

In order to understand the make-up of the sludge that is processed through the dryer, a brief description of the Stanadyne wastewater treatment system follows. The system is a conventional design by OMI Recovery Systems that has been operating since 1979. Included in the system are (Figure 1): A two-stage cyanide destruction unit, chrome reduction, equalization, pH adjustment for hydroxide precipitation, clarification with a Parkson Lamella, polishing with a Parkson DynaSand Filter and final pH adjustment prior to discharge into the Sanford municipal wastewater treatment system. A systematic elimination of chelators and other chemicals that could interfere with hydroxide precipitation is an essential part of the operational procedure that allows Stanadyne to achieve acceptable effluent quality. The success of the program has allowed the use of 50% sodium hydroxide for precipitation with only an occasional addition of calcium chloride to overcome precipitation problems. Additions of polyelectrolyte to facilitate flocculation and clarification are low with less than 100 pounds of dry material used in a year. The sludge that is generated by the system should be characterized as a caustic sludge.

Figure 1

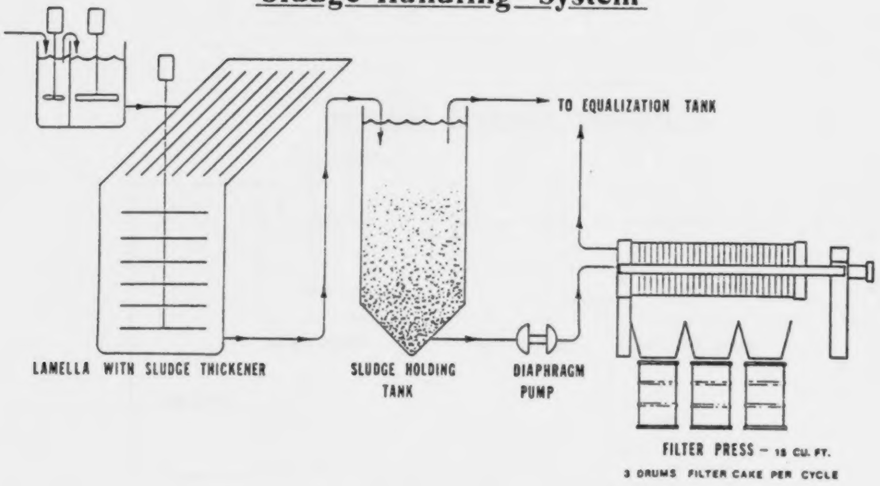
Pollution Control System


CAUSTIC
2 STAGE CYANIDE DESTRUCTION
CHROME REDUCTION
EQUALIZATION
NEUTRALIZATION
POLYMER
AIR
FLASHMIX & FLOCCULATION
pH ADJUST
DYNASAND FILTER
SLUDGE TO HOLDING TANK
LAMELLA GRAVITY SETTLER / THICKENER

Preparation of the sludge for disposal begins (Figure 2) when it is pumped from the sludge thickener on the Lamella to the sludge holding tank. The sludge is then mechanically dewatered in a 15-cubic-foot filter press. Analysis of the filter cake in 1982 and 1984 showed that the sludge was primarily composed of copper, nickel, chrome, zinc and iron with small amounts of cadmium, barium, lead and silver also present. The solids content averaged just under 25%. Since Stanadyne was pursuing a long-term goal of reduction in the volume of hazardous waste generated, the 75% moisture content of the sludge was considered a good candidate for significant volume reduction.

Figure 2

Sludge Handling System

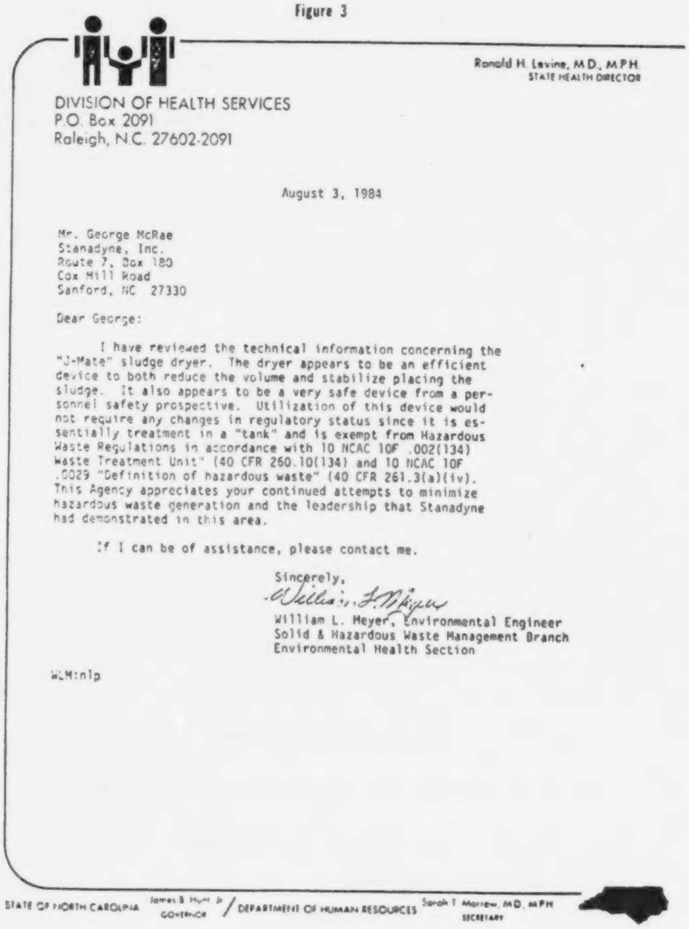

TO EQUALIZATION TANK
LAMELLA WITH SLUDGE THICKENER
SLUDGE HOLDING TANK
DIAPHRAGM PUMP
FILTER PRESS – 15 CU. FT.
3 DRUMS FILTER CAKE PER CYCLE

Although Stanadyne had been aware of the existence of sludge dryers for centrifuged sludge since 1981, efforts to acquire a dryer that would reduce the moisture content of the filter cake had been fruitless. At SUR/FIN '84 in New York City, the equip- now in use was introduced to the market. This equipment appeared to achieve the reductions that Stanadyne was looking for, and efforts to justify purchase of the dryer began.

Justification Process

The first step in Stanadyne's effort to obtain the dryer was sending literature describing the unit and its operation to the North Carolina Solid and Hazardous Waste Branch. Approval of the unit as an extension of the wastewater treatment system was a prerequisite to purchase since failure to get such a ruling could mean that the drying operation would be considered "treatment" and a part B, RCRA permit would be required. After review, the Hazardous Waste Branch sent a letter (Figure 3) that exempted the dryer from the Hazardous Waste Regulations.

Figure 3



Ronald H. Levine, M.D., M.P.H.
STATE HEALTH DIRECTOR

DIVISION OF HEALTH SERVICES
P.O. Box 2091
Raleigh, N.C. 27602-2091

August 3, 1984

Mr. George McRae
Stanadyne, Inc.
Route 7, Box 180
Cox Mill Road
Sanford, NC 27330

Dear George:

I have reviewed the technical information concerning the "J-Mate" sludge dryer. The dryer appears to be an efficient device to both reduce the volume and stabilize placing the sludge. It also appears to be a very safe device from a personnel safety prospective. Utilization of this device would not require any changes in regulatory status since it is essentially treatment in a "tank" and is exempt from Hazardous Waste Regulations in accordance with 10 NCAC 10F .002(134) Waste Treatment Unit" (40 CFR 260.10(134) and 10 NCAC 10F .0029 "Definition of hazardous waste" (40 CFR 261.3(a)(iv). This Agency appreciates your continued attempts to minimize hazardous waste generation and the leadership that Stanadyne had demonstrated in this area.

If I can be of assistance, please contact me.

Sincerely,
William L. Meyer
William L. Meyer, Environmental Engineer
Solid & Hazardous Waste Management Branch
Environmental Health Section

WLM:nlp

STATE OF NORTH CAROLINA James B. Hunt, Jr. GOVERNOR / DEPARTMENT OF HUMAN RESOURCES Sarah T. Morrow, MD, MPH SECRETARY

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The process of getting corporate approval for the purchase of a 5-cubic-foot dryer began in earnest after the regulatory hurdles had been cleared. Justification for purchasing the dryer were based on: a projected two-year payback; the need to meet waste minimization requirements; the specter of future disposal cost increases; the problem of availability and access to disposal sites; and the need to minimize long-term liability. The projected payback (Figure 4) was calculated using: a $50/drum disposal cost including transportation; $0/drum for disposal, since empty buffing compound drums were available; a 4-to-1 volume reduction; a $5/drum electrical cost; an estimated volume of filter cake of 130,000 pounds per year; 380 lbs. of filter cake/drum; and $22,000 for an installed dryer. With the above assumptions, the annual savings were estimated at $11,180 which resulted in a payback of about 2 years. The package was accepted by corporate and the dryer was ordered in March of 1985.

FIGURE 4

STANADYNE
Sanford, North Carolina

COST JUSTIFICATION REQUIREMENTS
FOR SLUDGE REDUCER

1. 4:1 VOLUME REDUCTION

2. AT A DISPOSAL COST OF $50/DRUM:
    4 X $50 = $200
        - 20 ELECTRICAL COST
        - 50 DISPOSAL COST
        $130 SAVED PER 4 DRUMS

3. AT A YEARLY SLUDGE PRODUCTION OF 134,000 LBS:
    134,000 ÷ 380 LBS/DRUM = 353 DRUMS
    353 ÷ 4 = 89 DRUMS
    89 X $130 = $11,570/YEAR

The dryer arrived in late August of 1985 after encountering delays at the manufacturer due to on-going design improvements. Installation of the dryer entailed moving the unit into place, installing I-Beams to raise the unit off the floor (Stanadyne preference), and hooking up the electricity. Only a $480 expense was incurred for installation. The start-up of the unit proceeded smoothly after the limit switches, which are part of the safety interlock system, were adjusted. The first drum of filter cake was dried on September 17, 1985.

Operation

Preparation for drying a load of sludge begins when a drum of filter cake (three are generated per press cycle) is moved from the press to the barrel-lifting mechanism on the dryer. The lid is hydraulically opened and the drum of filter cake (approximately 5 cubic feet) is hydraulically lifted and dumped into the unit. Limit switches must be activated by fully opening the lid or the barrel-dumping mechanism will not operate. The dryer will not operate if the limit switches on the barrel lifter are not met. This simple interlock system ensures safe operation. The drying cycle is initiated when the operator depresses the "run" button. Run times are controlled by a timer located on the control panel which allows the operator to control the degree of dryness achieved.

During the four-month period of operation, the average run time at Stanadyne has been 4.3 hours. The decision to run only 4.3 hours is based on ease of handling of the resulting dry sludge. Longer cycles and drier sludge can be achieved, but the dried sludge can become very dusty, presenting housekeeping and potential health problems. The dried sludge is unloaded from the unit by gravity into a drum which is then labeled and prepared for disposal.

Dust Collector

The dust collector is an essential element in the operation of a dryer. Longer drying times result in production of increased amounts of fine dust. In recognition of the importance of the dust collector, the manufacturer has increased the size of the dust collector which is supplied as a standard part of the equipment. Moist air that is generated in the drying process should be vented to the outside.

Program Results

The first four months of operation of the dryer at Stanadyne-Sanford have yielded excellent results. The decision to begin operation with drying times of 4.3 hours has resulted in the production of a granular material with the solids content increased from 23% to 49%-62%. A volume reduction of 66.7% and a weight reduction of 63.2% were achieved when the solids content of the granular material was increased to 62%. (Variability in the total solids in the filter cake and the drying time will affect the reductions which can be achieved. Optimization should be evaluated for each application.) The projected 4-to-1 sludge reduction and higher solids content could be achieved with the installation of the larger dust collector which is now standard with the unit. This improvement is now underway but the results will be too late for this paper.

Although the projected 4-to-1 reduction in sludge volume has not yet been achieved, increases in disposal cost and changes in the buffing process that eliminated our source of free empty drums resulted in an improved payback. The stricter hazardous waste landfill operational requirements that came into effect with the RCRA reauthorization have resulted in a 39% increase for the disposal of a solid metal hydroxide sludge at the GSX landfill in Pinewood, South Carolina. The specter of future disposal cost increases loomed larger and faster than envisioned in the justification for the dryer and our fears were confirmed when disposal cost increased from $36/drum to $50/drum. The cost for disposal alone, when the South Carolina waste disposal tax is included, totals $54/drum. Changes in the way the buffing compound was purchased resulted in the elimination of our source of free empty drums. Purchase of reconditioned DOT-approved drums in North Carolina can run as high as $20/drum. Fortunately, Stanadyne-Sanford was able to purchase reconditioned drums through Stanadyne-Elyria, Ohio at $7/drum. Transportation costs were lowered by changing hazardous waste haulers, but this cost remained highly variable depending on the success of cooperative shipping with other local industries. The average transportation cost was $9/drum. The projected total cost for the drying equipment of $22,000 was "right on the money" with total cost, including purchase price, freight and installation, totaling $21,979 (Figure 9). Using the figures of $54/drum for disposal, $9/drum for transportation, $7/drum for the disposal drum, $5/drum for electricity, 134,000 lbs. of filter cake generated in 1985, 380 lbs./drum of filter cake, a 3-to-1 reduction, and an installed price of $21,979 for the dryer, a cost savings of $14,750/year (Figure 5, Table VI) would have been achieved in 1985 with a payback of 1.49 years (Figure 6, Table VI).

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Figure 5

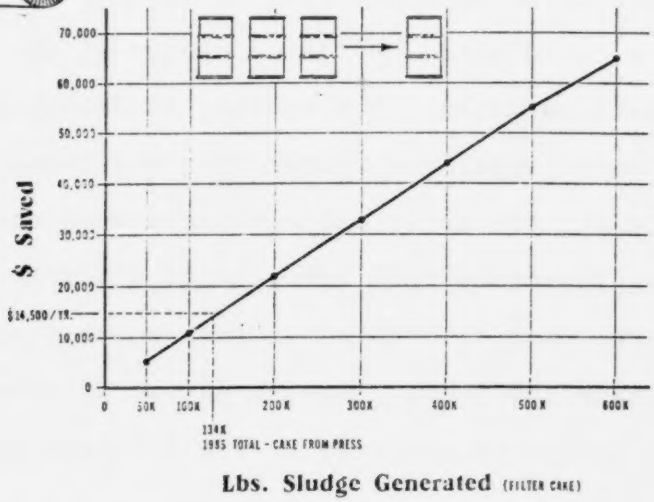


Figure 6

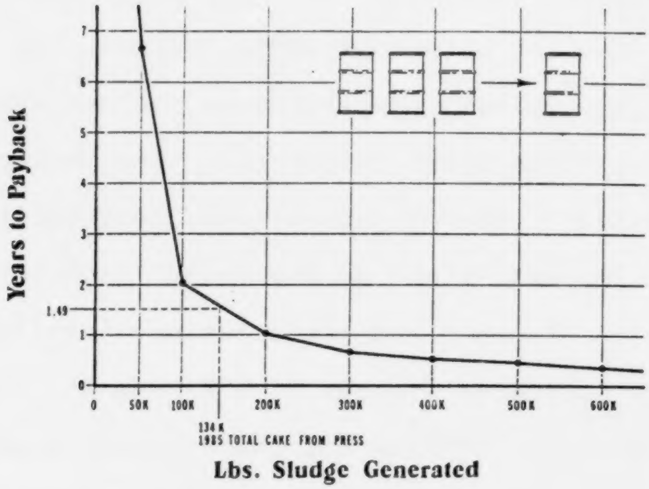


TABLE VI

STANADYNE ANNUAL DISPOSAL COST SAVINGS WITH DRYER

Lbs./Yr.	(Barrels X Cost/BBL)	Disposal Cost Before Drying/Yr.	(BBL's X Cost/BBL)	Disposal Cost After Drying/Yr.	Savings/Yr.	Payback (Yrs.) At Current Price	Payback (Yrs.) At Orig. Price
600,000	1560 X 70	109,200	520 X $85	44,200	65,000	.43	.34
500,000	1300 X 70	91,000	433 X $85	36,805	54,195	.52	.41
400,000	1039 X 70	72,730	346 X $85	29,410	43,320	.65	.51
300,000	779 X 70	54,530	260 X $85	22,100	32,430	.86	.68
200,000	520 X 70	36,400	174 X $85	14,790	21,610	1.30	1.02
100,000	260 X 70	18,200	87 X $85	7,395	10,805	2.59	2.03
50,000	130 X 70	9,100	44 X $85	3,740	5,360	8.48	6.66

CURRENT PRICE: $28,000

ORIGINAL PRICE: $21,979*

*(Freight and installation included.)

Figure 9

Purchase Price	**$21,200**
Freight	**$ 299**
Installation	**$ 480**
Total cost	**$21,979**

Disposal cost	**$54 /drum**
Transportation	**$9 / drum**
Drum cost	**$7 / drum**
	$70 / drum
Electrical cost	**$5 / drum**

Electrical Usage

The one problem involved with the unit and sludge drying in general is the cost of the energy. The dryer purchased by Stanadyne is all electric with three main areas requiring electric power: the heaters, the motor and the blower on the dust collector. The design specification for the heaters is 13.5 KW; for the motor, 8 KW; and for the blower, .8 KW. In running a tape, measuring current draw on the motor that runs the plows, the actual power usage was 4.9 KW. The power consumption therefore totaled 13.5 + 4.9 + .8 or 19.2 KW for 4.3 hours at a cost of $.0581/KW-H or $4.80/load.

A cost of $5/load was used in payback calculations for the Stanadyne dryer. A table (Table II, Figure 11) is included showing the effect on money saved and years to payback of electrical cost ranging from $5/load to $10/load. The percentages of overall disposal cost for electricity for drying will decrease as the cost of landfilling increases.

TABLE II

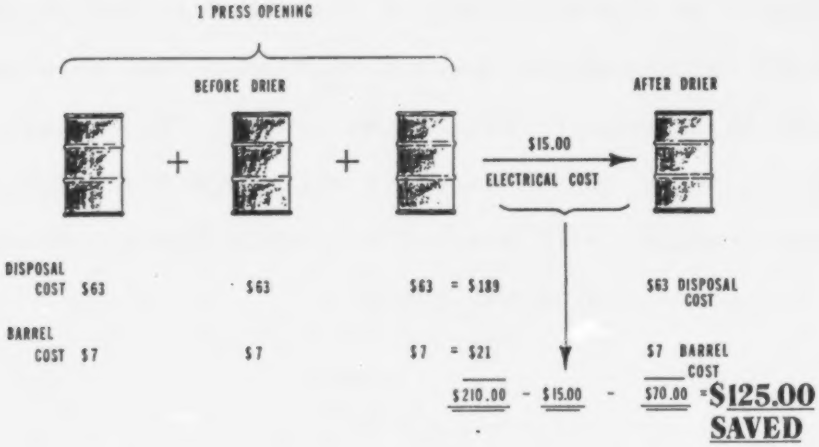
$ SAVINGS AND PAYBACK

FOR $5-$10 ELECTRICAL COST PER LOAD

		$ SAVED	PAYBACK
$5/Load:	$210 - 15 - 70 = $125 X 118 =	$14,750	1.49 Years
$6/Load:	$210 - 18 - 70 = $122 X 118 =	$14,396	1.53 Years
$7/Load:	$210 - 21 - 70 = $119 X 118 =	$14,042	1.57 Years
$8/Load:	$210 - 24 - 70 = $116 X 118 =	$13,688	1.61 Years
$9/Load:	$210 - 27 - 70 = $113 X 118 =	$13,334	1.65 Years
$10/Load:	$210 - 30 - 70 = $110 X 118 =	$12,980	1.69 Years

Figure II

Disposal Cost Comparison


1 PRESS OPENING
BEFORE DRIER
AFTER DRIER
+
+
$15.00
ELECTRICAL COST
DISPOSAL COST $63
$63
$63 = $189
$63 DISPOSAL COST
BARREL COST $7
$7
$7 = $21
$7 BARREL COST
$210.00 - $15.00 - $70.00 = $125.00 SAVED

EP Toxicity

Analysis of the dried sludge using EP Toxicity procedures indicates that the stability of the sludge has improved. When the EP Toxicity test was performed on the filter cake in April of 1982 (Table III), the sludge leached cadmium and lead at levels which exceeded the maximum allowable concentrations. Chromium leached out at levels of 2.05 mg/l (limit is 5 mg/l) despite its low concentration in the sludge sample. The December 1985 sample was tested using the standard EP Toxicity procedure and also with the new EPA draft "Toxicity Characteristic Leaching Procedure (Method 13 XX)". Although levels of chromium and lead found in the sludge sample were significantly higher than in the 1982 sample and cadmium was at about the same level, all three metals passed both leaching tests. The levels for cadmium and lead were undetectable using both methods while chromium registered levels of .12 mg/l using the standard method and 1.85 mg/l using the draft method as compared to a maximum limit of 5 mg/l. (See Table IV.) The results of the leachate tests on this one sample indicate that the stability of the dried sludge in regard to acid leaching has improved; however, Stanadyne has no plans at the present to attempt to delist the sludge. The future changes which may occur in the leaching procedure test emphasize the dangers involved with delisting a waste under present standards when future standards may change.

TABLE III

STANADYNE
Sanford, North Carolina

SLUDGE ANALYSIS - APRIL 1982

Sludge Analysis/25% Solids	(mg/kg)	EP Toxicity	Limit mg/l
Cu	33,000		
Zn	12,200		
B	131		
Ni	5,000		
Cr	90	2.05 mg/l	5.0
Ba	1.66		
Cd	180	4.65 mg/l	1.0
Pb	278	5.30 mg/l	5.0
Ag	.54	<.01 mg/l	5.0

TABLE IV

SLUDGE ANALYSIS - DECEMBER 1985

Sludge Analysis 49% Solids	(mg/kg)	EP Toxicity SW-846 Method 1310	Toxicity Characteristic Leaching Procedure EPA Draft Method 13XX
Cu	224,000		
Zn	40,000		
Ni	30,000		
Cr	38,200	.12 mg/l	1.85 mg/l
Pb	2,000	<.005 mg/l	<.005 mg/l
Cd	100	<.01 mg/l	<.01 mg/l
Fe	7,400		

Pollution Prevention Program

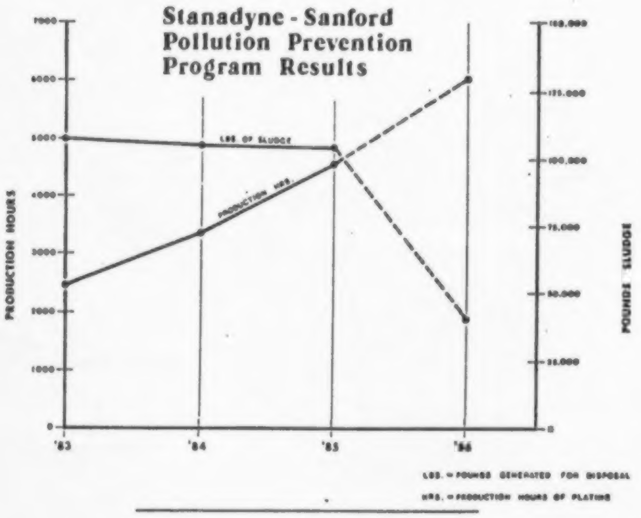
Stanadyne-Sanford began its comprehensive program of in-process waste reduction in 1983. The accompanying table (Table V and Figure 7) shows a steady decrease in pounds of waste generated per production hour in plating. (Waste is also generated in brite dipping, but production hours were not factored in and have remained fairly constant.)

Table I

Stanadyne - Sanford
Pollution Prevention
Program Results

	YEAR	TOTAL LBS/HRS.	LBS. PER HOUR
P.P.P. PROGRAM STARTED →	1983	115,000 / 2,380	48.3
	1984	111,000 / 3,293	33.7
SLUDGE DRIER INSTALLED →	1985	110,000 / 4,550	24.2
	1986 (PROJECTED)	40,000 / 6,000	6.7

Figure 7



Stanadyne - Sanford
Pollution Prevention
Program Results

LBS. = POUNDS GENERATED FOR DISPOSAL
HRS. = PRODUCTION HOURS OF PLATING

Stanadyne's success in making "pollution prevention pay" through in-process waste reduction, coupled with the use of the sludge dryer to reduce end-of-pipe waste volumes, has resulted in significant reduction in waste shipped off-site for disposal per production hour. Stanadyne's pollution prevention program has been recognized by being awarded the Governor's Award of Excellence in Hazardous Waste Management in 1983 and has recently received the award again for 1985.

As the volume of waste shipped off-site has been reduced, the need for cooperative efforts in shipping waste to achieve economical transportation cost has increased. The formation of the Lee County Waste Manager's Association (Figure 8) has helped facilitate shared loads for hazardous waste shipments. The reduced cost of truck load rates as opposed to less than truck load rates has benefited association members.

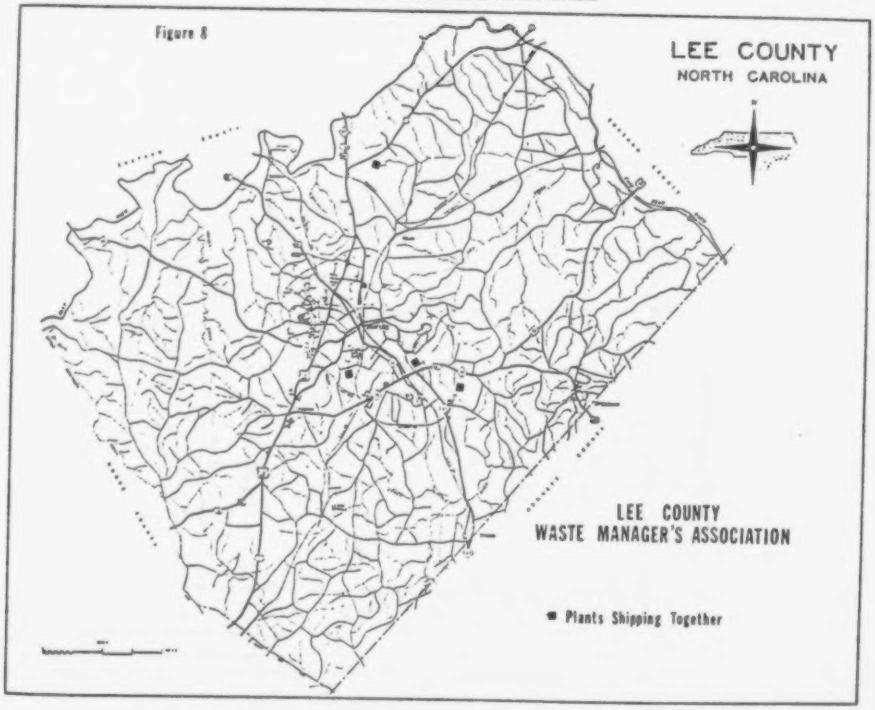


Figure 8

Conclusion

Stanadyne's Sludge Reducer has met or surpassed the expectations expressed during the justification of the unit. A 1.49 year payback was achieved and the impact of increases in disposal cost reduced. The new waste minimization requirements are clearly met and the significant volume reductions and the resulting increase in metal content improve the economics of sludge shipment over greater distances for disposal and improve the feasibility of recovery. Last, but not least, is the issue of long-term liability. Reductions in volume and increase in sludge stability as measured by the EP Toxicity Test should result in decreased long-term liability.

The results of the first four months of sludge dryer operation at Stanadyne have shown clearly that the unit will make a significant contribution to Stanadyne's long-term goal of reducing the amount of hazardous waste shipped off-site.

NOVEL, SYNTHETIC COMPOUNDS FOR THE EFFICIENT REMOVAL OF NICKEL AND ZINC FROM PLATING EFFLUENT

Dr. D. Brener, V.P. Sales and Bus. Dev., and Dr. C.W. Greer, Mgr. Applications Dev., DeVoe-Holbein Canada Inc., Dorval, Quebec; S.G. Nelson, Pres., Sanitech Inc; Twinsburg, Ohio.

ABSTRACT

Two case studies are presented on an efficient, effective and economically attractive means of reduction and subsequent elimination of toxic heavy metals from electroplating effluents. The first study describes the removal of Zn from a captive plating operation. The modular wastewater treatment unit processes 24,000 gallons of effluent per week, containing 10 to 300 ppm Zn, and is discharging treated water containing less than 1ppm Zn. Daily regeneration of the treatment unit produces a metal concentrate of typically, 50,000 ppm Zn. The second case study describes the effective removal of Ni (130-180ppm) from plating rinsewater.

INTRODUCTION

Current Environmental Protection Agency regulations and impending rulings on effluent discharge and sludge disposal have forced industry to re-evaluate their wastewater treatment processes. The discharge of toxic heavy metals has become subject to stringent guidelines and intense scrutiny by authorities. Although much of this type of pollution can be reduced (i.e. in volume) through increased process control, these measures do not eliminate heavy metals from wastewaters.

Traditional methods of dilution and discharge of heavy metal wastes from industry are now regarded as unacceptable and there is a need to implement some form of wastewater treatment technology. The technology must not only be effective in reducing metals to the required limits but must also achieve this goal economically. The metal finishing industry, according to available statistics,[1] is responsible for about 57% of all metal discharged in effluents. A variety of waste treatment technologies have previously been utilized in the metal finishing industry[2] with varying degrees of success for metal extraction, cost effectiveness, and potential long term benefits. A recently developed technology the "DeVoe-Holbein Process" has distinct advantages over existing technologies for the treatment of wastewaters from the metal finishing industry.

This paper describes two specific cases in which this wastewater treatment process has been implemented to efficiently and economically clean-up toxic wastewaters. In both cases the treated effluent is discharged directly to sewer.

DeVoe-Holbein media are used in a manner not unlike classical ion exchange (Fig. 1). The media is contained in a fixed bed and the metal-laden solution is passed through the media during the service cycle. As the solution travels through the media, the metal is captured. Following saturation, the bed is backwashed and the bound metal is efficiently displaced by passing the appropriate regenerant through the media .

This wastewater treatment process is not a high pressure process permitting versatility in column dimensions and configuration. Co-current and counter-current fixed bed systems have been employed. The versatility of the basic modular system (Fig. 2.) can be easily expanded or realigned to reflect the end users' current and future needs.

The proprietary composition used in this process enables selective, high efficiency and high capacity capture of the target metals. Sequential recovery of various metals from a complex solution can be attained. Target metals in treated wastewaters are typically in the parts per billion range. Fluctuating hardness of the water source does not compromise efficiency of capture of the target metal by the composition. This, along with the ability to process at high flow rates enables the end user to minimize his capital and operating costs.

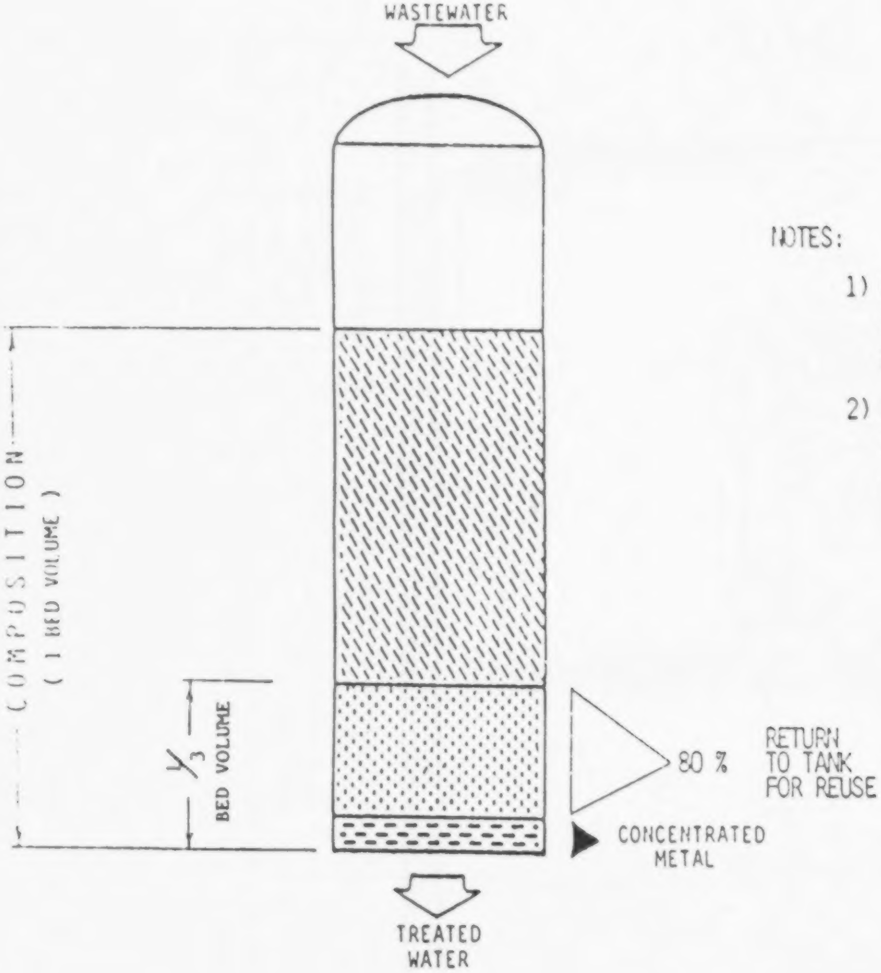
To demonstrate the broad range of applications of this wastewater treatment process to industry, two specific field cases are presented. The sources of wastewater are from a dedicated captive plating operation with very high quality control specifications and from a relatively large multi-purpose electroplating job shop. The nature of the wastewater effluent, the wastewater treatment system and the performance characteristics therefrom are described.

CASE STUDY # 1

A manufacturer of high quality sophisticated technical products operates a dedicated (single product) zinc chloride electroplating process. This automatic rack plating operation is captive to ensure stringent quality control standards are met. The basic operational flow of the process is depicted in Figure 3. The plating tanks are followed by a series of counterflow rinse tanks, the first of which produces wastewater effluent at a rate of 5 gpm. The wastewater is collected in a holding tank, which then becomes the feed solution to the wastewater process unit.

Typical wastewater characteristics and production rates are shown in Table I. The objective of implementing the wastewater treatment process was to maintain a zinc level, in the discharge, at less than 2 ppm, and never exceeding 5 ppm.

The wastewater process unit (Fig. 2) was designed to operate on a 16 hour cycle, with the influent zinc concentration ranging from 50-300 ppm. At the end of the operating day (16 hours) the process unit is

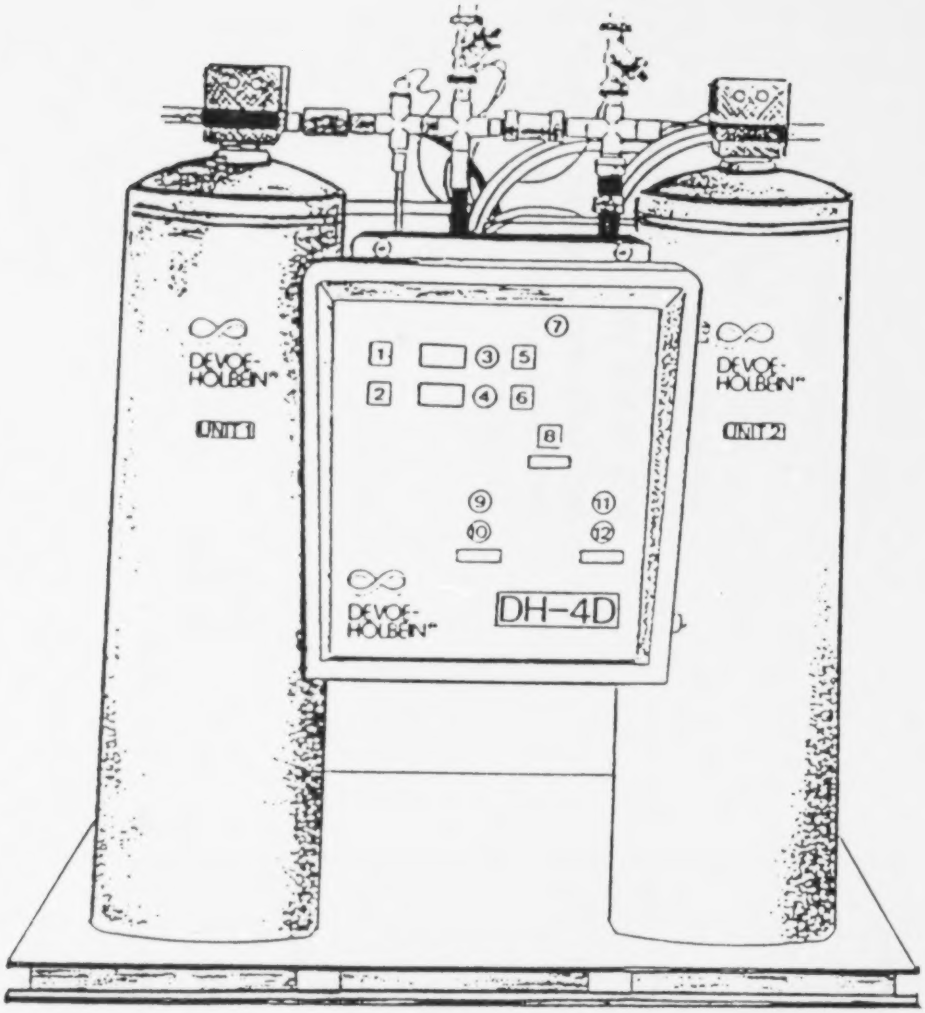

WASTEWATER
COMPOSITION
(1 BED VOLUME)
1/3 BED VOLUME
80 %
RETURN TO TANK FOR REUSE
CONCENTRATED METAL
TREATED WATER

NOTES:

1) ONLY 1/3 BED VOLUME OF DILUTED REAGENT REQUIRED TO REGENERATE DEVOE-HOLBEIN COMPOSITION.

2) FRESH WATER RINSE CHASES OUT CONCENTRATED METAL TO RECOVERY TANK FOR REUSE.

FIGURE 1. WASTEWATER PROCESS UNIT COLUMN SHOWING REGENERATION


DEVOE-HOLBEIN
UNIT 1
1
2
3
4
5
6
7
8
9
10
11
12
DEVOE-HOLBEIN
DH-4D
DEVOE-HOLBEIN
UNIT 2

1. Regeneration Selector: Unit 1
2. Regeneration Selector: Unit 2
3. LED Holder (Optional)
4. LED Holder (Optional)
5. Regeneration Indicator: Unit 1(Yellow)
6. Regeneration Indicator: Unit 2(Yellow)
7. Regeneration Status Light (red)
8. Regeneration Start Button
9. Filter Alarm Status Light (red)
10. Alarm Defeat Switch
11. Main Power Status Light (green)
12. Main Power Switch

FIGURE 2. WASTEWATER PROCESS MODULAR UNIT

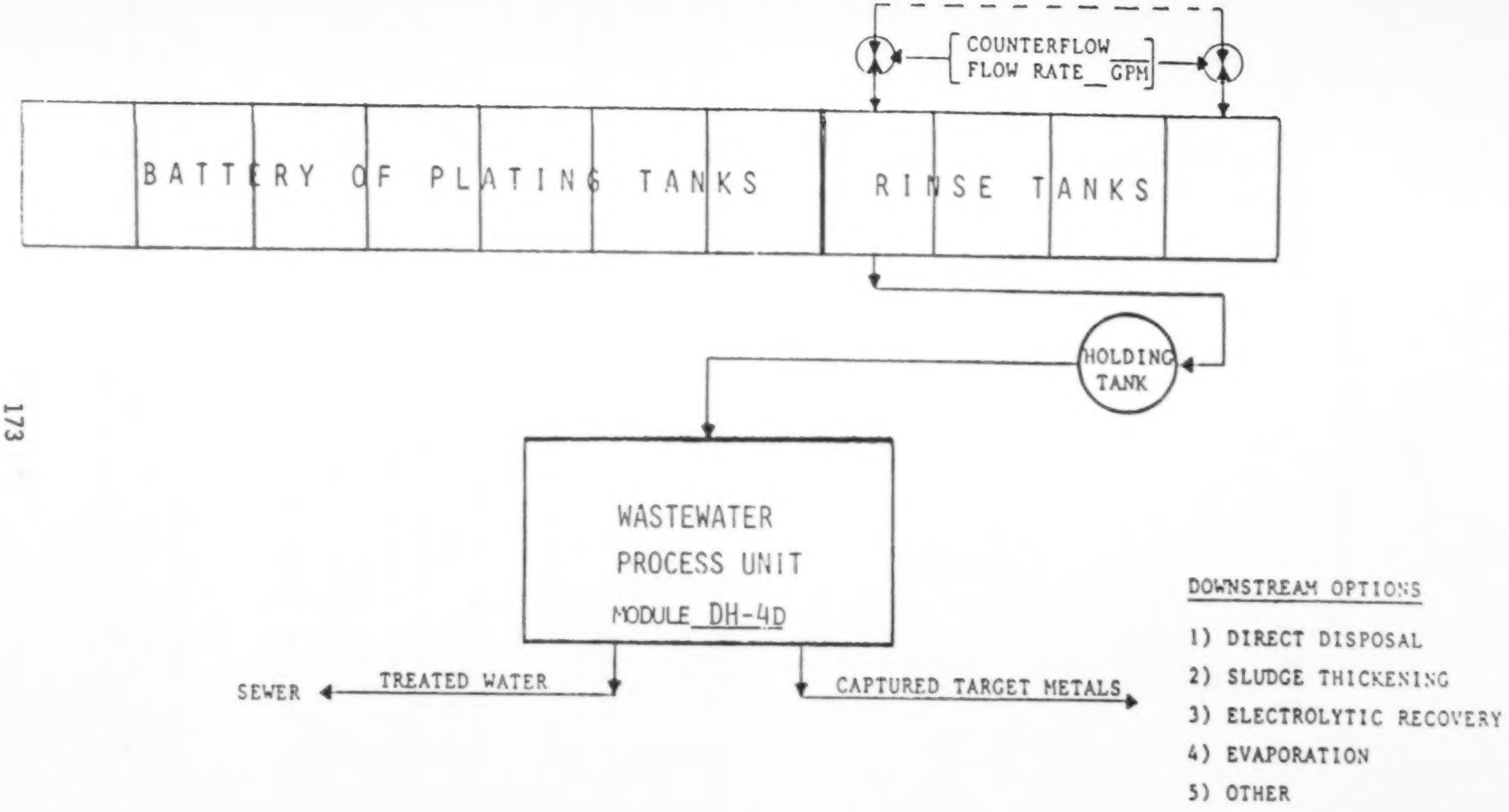

COUNTERFLOW
FLOW RATE __ GPM
BATTERY OF PLATING TANKS
RINSE TANKS
HOLDING TANK
WASTEWATER
PROCESS UNIT
MODULE DH-4D
SEWER
TREATED WATER
CAPTURED TARGET METALS
DOWNSTREAM OPTIONS
1) DIRECT DISPOSAL
2) SLUDGE THICKENING
3) ELECTROLYTIC RECOVERY
4) EVAPORATION
5) OTHER

FIGURE 3. WASTEWATER TREATMENT OF RINSEWATER FROM A ZN ELECTROPLATING OPERATION

TABLE I

Zn-wastewater characteristics

ELEMENT	CONCENTRATION (ppm)
Zn	192.6
Mn	0.05
Mg	8.54
Na	43.4
Sr	0.16
B	18.4
Si	1.2
Ca	39.9

pH	∿ 6.3-7.3
gpm	5
hpd	16
dpw	5

regenerated and reconditioned. Figure 4 shows the results of the operation of the wastewater process unit over a two week period. The concentration of Zn in the wastewater influent to the process unit varied significantly, depending on the extent of the plating operation on a given day. The influent concentration of the target metal (Zn) ranged from 10 ppm to as high as 280 ppm over the period examined. Zn concentration in the treated effluent from the wastewater process unit was below 1 ppm.

The process unit was regenerated daily following the 16 hour processing period (Fig. 1). Less than one third of a bed volume of regenerant is applied at a reduced flow rate (0.5 bed volumes per hour) and chased with a water rinse, also at the reduced flow rate. The bound Zn is removed within one bed volume (as little as one third of a bed volume) of regenerant, and is directed to the metal recovery tank. Metal concentration in the regenerant is typically 50,000 ppm (can reach as high as 100,000 ppm) facilitating re-use of the metal concentrate.

CASE STUDY # 2

A large job shop operating four different processes, and using at least eight different metals, services a large clientele for many of their electroplating requirements (Fig. 5) . Presently, spent baths, acids and soaps are sent to landfill. Effluents are pH adjusted in a neutralization

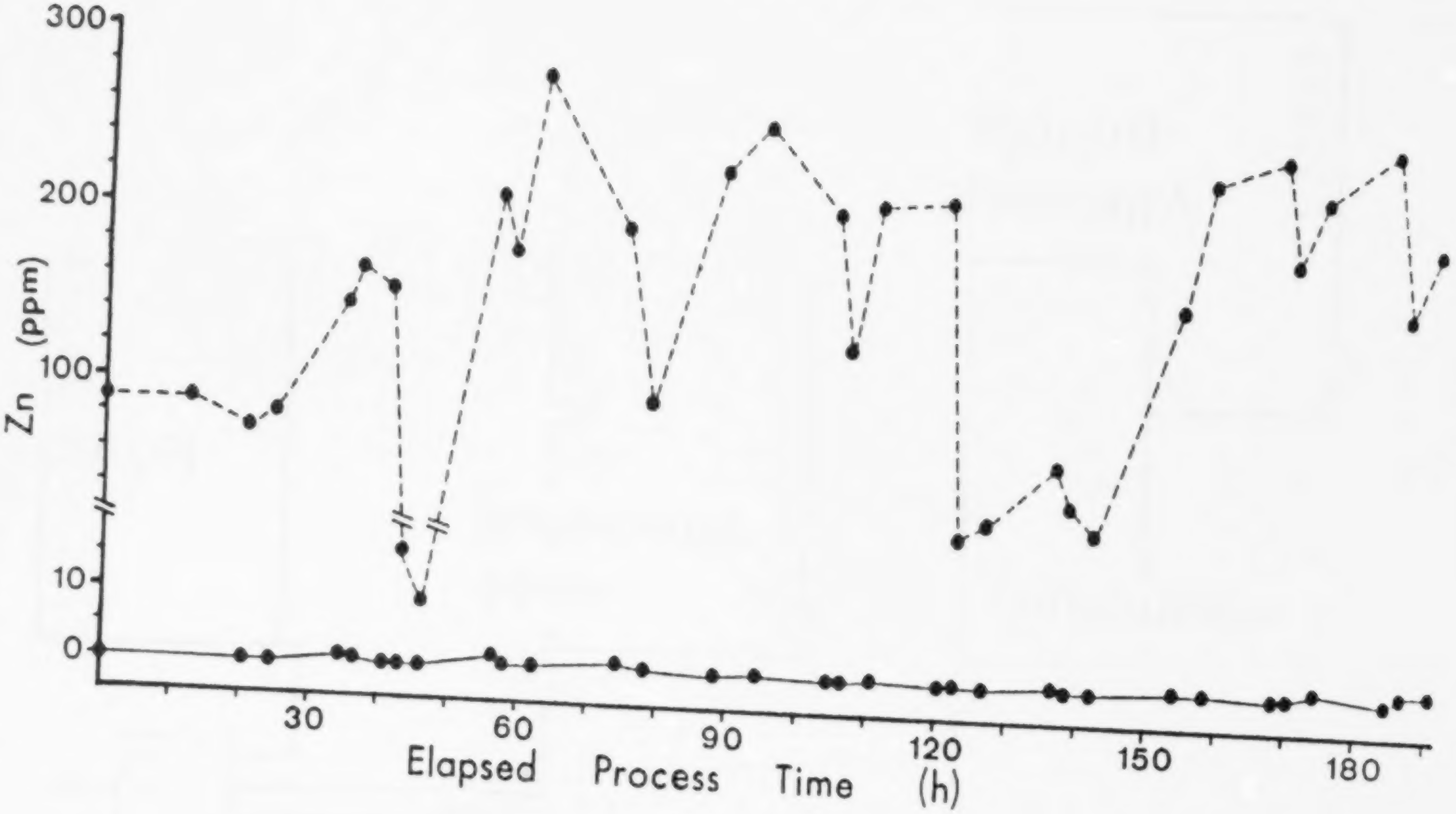


FIGURE 4. REMOVAL OF ZN FROM ELECTROPLATING WASTEWATER
WASTEWATER INFLUENT (●--●), TREATED EFFLUENT (●—●)

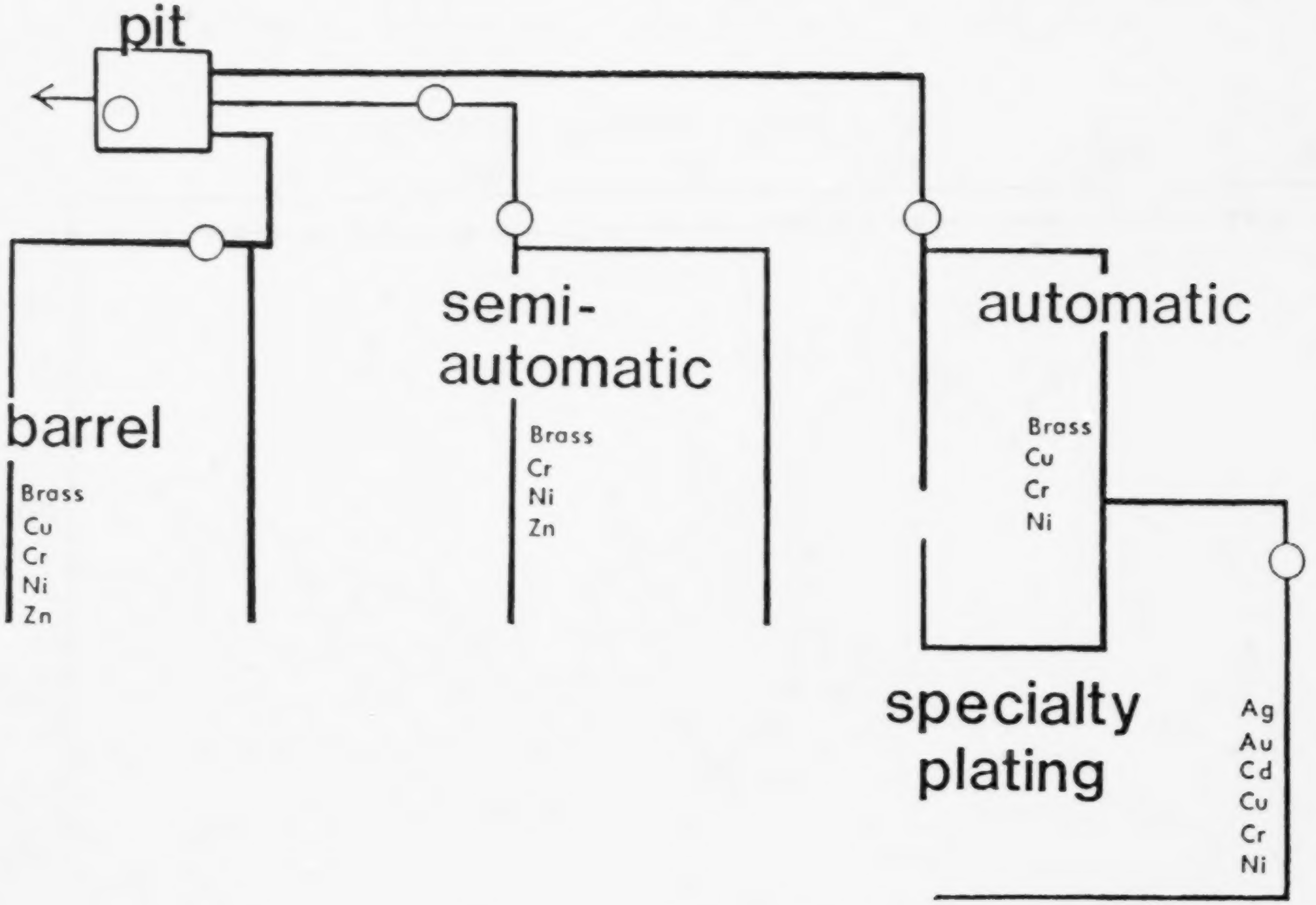

pit
barrel
Brass
Cu
Cr
Ni
Zn
semi-automatic
Brass
Cr
Ni
Zn
automatic
Brass
Cu
Cr
Ni
specialty plating
Ag
Au
Cd
Cu
Cr
Ni

FIGURE 5. ELECTROPLATING JOB SHOP OPERATION

TABLE II

Ni-rinsewater characteristics

ELEMENT	CONCENTRATION (ppm)
Ni	136.6
Zn	0
Fe	1.75
Mn	0.26
Mg	3.06
Cu	0.08
Na	71.7
Sr	0.07
B	14.8
Si	2.9
Ca	14.1
Cr	0
Al	0
Cd	0

pH 6.5

pit, and discharged directly to the sewer. Direct discharge of rinse effluents is no longer possible, and wastewater treatment processes must be implemented.

The wastewater process unit successfully treats both the individual and the combined wastewater effluents (which may contain cyanide) containing nickel, zinc, brass, chrome and precious metals. To demonstrate the efficiency of the wastewater treatment system, a case study of the nickel rinse effluent from the automatic rack plating operation (Fig. 5) was undertaken. Although combined effluents are treated efficiently, treatment of individual rinse lines offers several advantages over treatment of the combined effluent. Smaller treatment systems are required for individual rinsewater effluents, and these can be operated in a closed loop cycle where treated rinsewater is re-used. This system ultimately reduces the volume of fresh rinsewater required, and when the process unit is regenerated the target metal can be recovered in a higher purity concentrate.

The data in Figure 6 shows the results of the operation of the nickel rinsewater treatment system over two complete cycles of loading and regeneration. The nickel concentration in the rinsewater effluent varied from 130 ppm to 180 ppm. The treated rinsewater contained less than 1 ppm of Ni, and when the Ni concentration in the effluent of the process unit reached approximately 5 ppm, the unit was regenerated. The regenerant solution contained highly concentrated Ni, in less than two bed volumes.

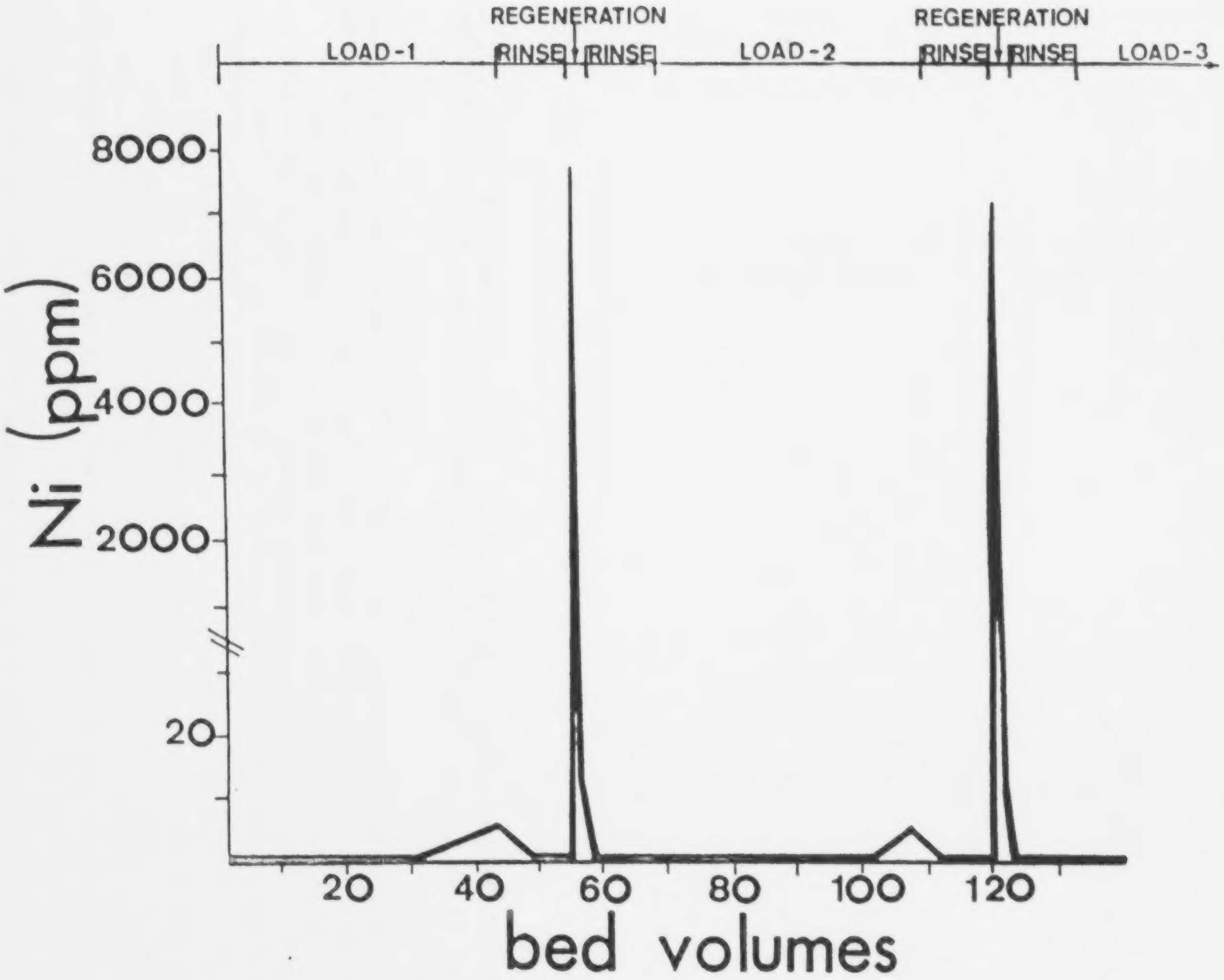


FIGURE 6. REMOVAL OF NI FROM ELECTROPLATING RINSEWATER, AND REGENERATION OF WASTEWATER TREATMENT UNIT

CONCLUSION:

The DeVoe-Holbein wastewater treatment process has been shown to be a versatile, highly efficient and economic answer to the treatment of wastewater from the metal finishing industry. The case studies demonstrated the efficient and reliable treatment of the fluctuating levels of metal, typically found in rinsewaters from operating electroplating processes. Treated water is free of target metal (s) and recovery of target metal (s) after regeneration is high (50,000 ppm). Closed-loop systems, whereby direct reuse and/or further processing of recovered metal and treated water is a practical option, are available to end-users of these wastewater treatment systems.

References:

[1] EPA, February, 1982. Assessment of the Impacts of Industrial Discharges on Publicly Owned Works. NTIS No PB-153958.

[2] Cherry, K.F. 1982. Plating Waste Treatment. Ann Arbour Science Publishers Inc., USA.

RECYCLING IS THE ANSWER FOR WASTEWATER TREATMENT

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Minneapolis, MN 55431

The pollution of the environment by industrial processes has generated enforcement of pollution standards and the development of pollution control equipment in many countries all over the world. Because of strong legal regulations, waste water treatment and recycling in the metal finishing industry became, within the last ten years, a necessity for operating a plating facility in West Germany.

One of the latest successful developments is the RMA-System (recovery of metals from waste water) which offers the electroplating and printed circuit board industries rinse water purification combined with the reclamation of metals by means of portable ion exchangers [1, 2, 3]. This system was started in 1979 as a pilot project sponsored by the West German Federal Ministry for Research and Technology.

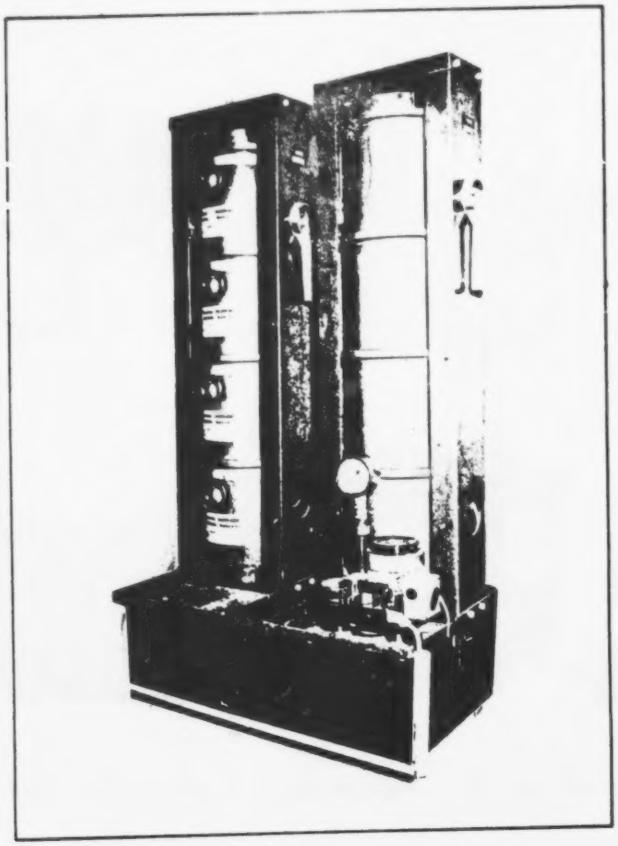

fig. No. 1:
RMA-columns

Today, more than 200 plating companies are using a special service system and a central recovery facility (CRF), operated by a private company called INOVAN.

The RMA system utilizes a column, or series of columns, each consisting of four cartridges containing a resin through which water from a rinse tank is pumped to absorb metals as well as non-metallic substances (see fig. No. 1).

Two basic types of resin are used for the ion-exchange:

1. A cation exchange resin to absorb the metals.
2. An anion exchange resin to absorb the non-metallics.

Using a single column as an example, there are two cartridges for the cation resin and two for the anion resin. This type of design generates deionized water from rinse water. The equipment uses the upstream technique. Therefore, the bottom cartridge becomes loaded first (this is indicated by a visual load indicator) and is removed for regeneration and reuse. The top cartridge takes its place and a regenerated cartridge is added.

After the regeneration of the cartridge, the regenerants can be used for recycling.

A large chromium plating company located in Minneapolis, MN, installed the RMA-equipment in order to meet governmental standards. Because there is no CRF present, this company built their own regeneration plant and developed their own recovery systems. (see fig. No. 2).

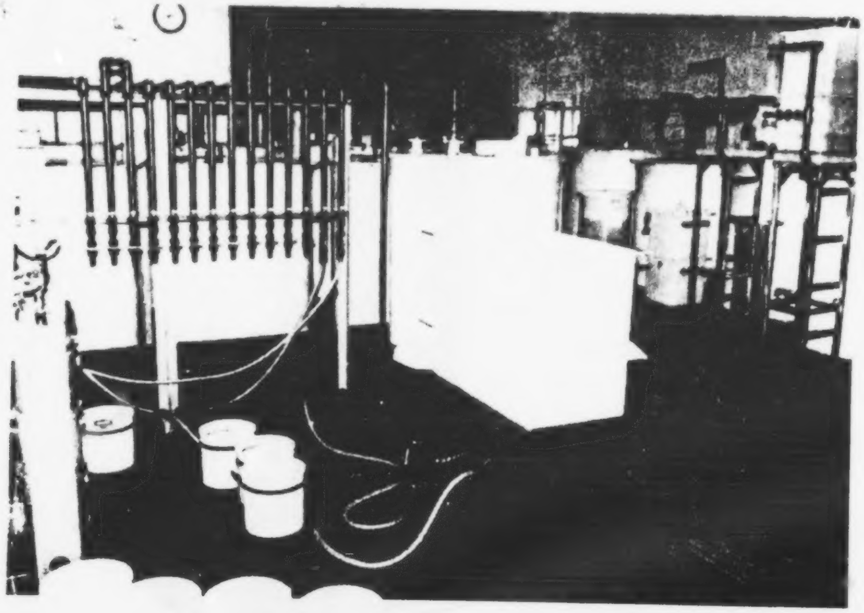

fig. No. 2: Regeneration & recycling room

The operation and function of this new regeneration and recycling facility is described in the remainder of the report.

Rinse water recirculation with ion exchange

RMA-columns are installed adjacent to all rinse systems behind each plating bath, including Copper, Nickel and Chromium. The overflow of the rinses goes into the bottom reservoir of a RMA column upstream through the ion exchange bed and from the column back into the rinse tank as deionized water. (see fig. No. 3).

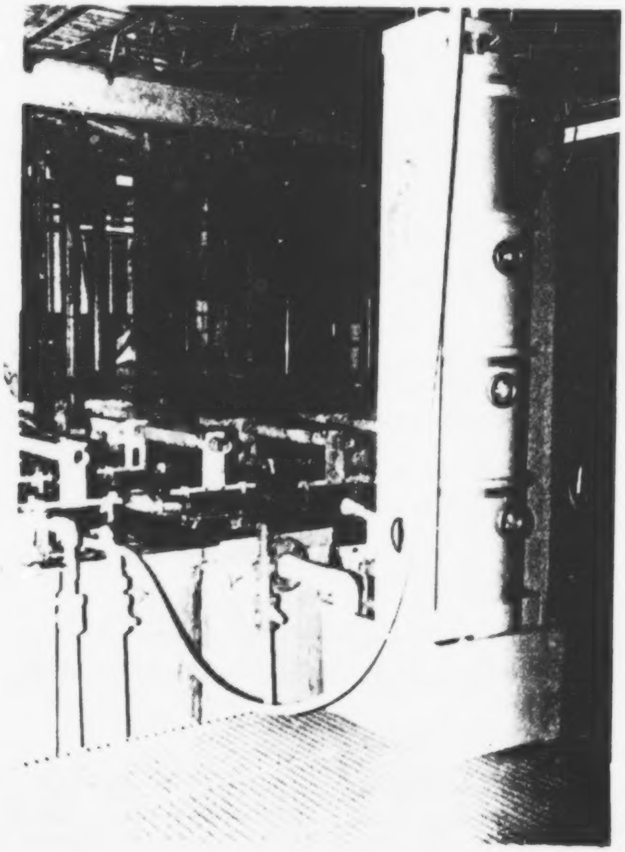

fig. No. 3: Rinse water circulation with an RMA-column

In most cases the preferred rinse system is a combination of a stagnant rinse (dragout) and a flowing rinse or counterflow rinse:

* Because of the rinse water circulation, there are water savings of up to 80% in this plant.
* The stagnant rinse can be used directly for recycling (i.e. replenishing a bath, evaporative recovery, reverse osmosis, etc.) and therefore it is changed weekly.
* The drag in of electrolyte from the stagnant rinse into the flowing rinse system has a low concentration of metal, allowing an efficient operation of the ion exchangers on the flowing rinse.

When the cartridges are loaded, they are exchanged and regenerated. The resulting regenerants are collected in separate holding tanks for reuse in a new regeneration cycle, or for reclamation of the metal.

Table No. 1 shows the operation data of the used ion exchange systems.

Flow rate	0 to 5 gpm
Volume of resin	2 cubic ft.
Capacity of resin	up to 80 equiv.
Max. specific flow rate	80 gph per cubic ft. of resin
Requirement of regenerant	10 to 30 gals per cub. ft. of resin
Weight (filled with resin)	225 lbs
Floor space	3.2 sq. ft.
Height	5 ft. 10 in.

Table 1: Operational data of an ion exchange column

Evaporative recycling of chromic acid

The regenerants and the dragout of the chromium plating line are collected together in a special storage tank. From there they are pumped through an ion exchange column which is filled with cation exchange resin to remove the impurities from the solution, which are sodium (from the regenerants), trivalent chromium and other metals (from the plating process). After the purification of the chromic acid the solution is pumped into an atmospheric evaporation system spray tower to concentrate the solution up to bath concentration. (see fig. No. 4).

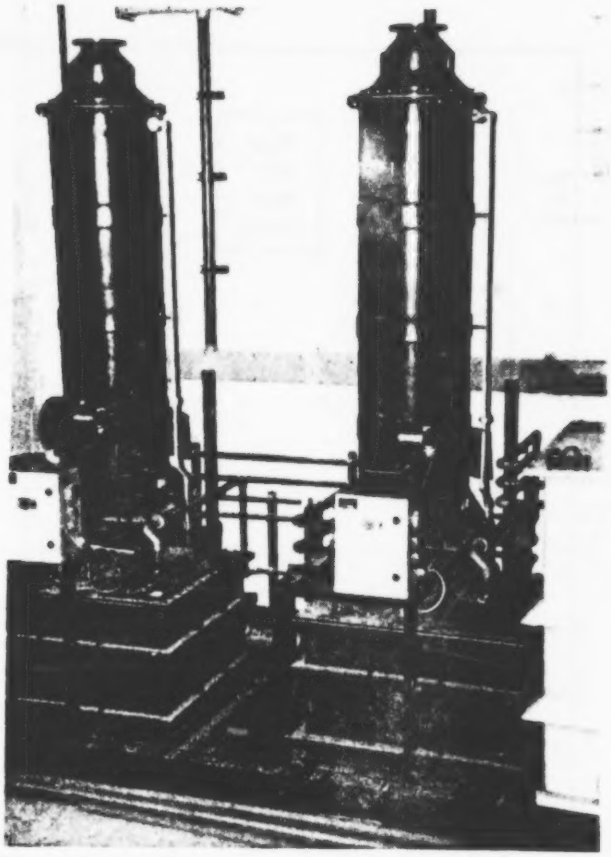

fig. No. 4: Spray towers

The spray tower is operating at 140° F and evaporating 7 gph of water. The concentration concerning chromic acid (CrO_3) of the dragout/regenerant solution is 28% of bath concentration. Approximately 700 gals per week of this solution have to recovered. The evaporative process takes about 3 days to generate 200 gals of chromium plating bath.

Fig. No. 5 shows a flow scheme of the recycling process of chromic acid.

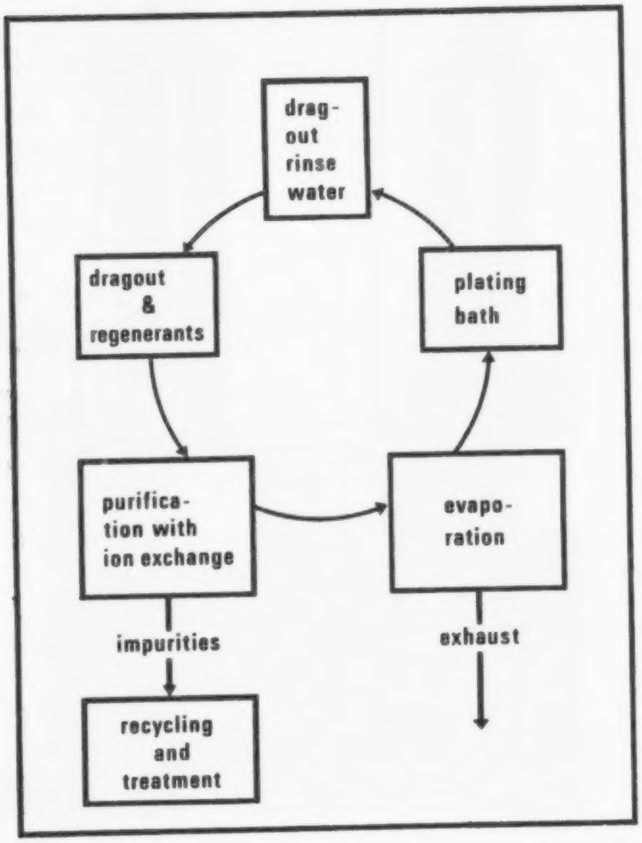
drag-out rinse water
dragout & regenerants
plating bath
purification with ion exchange
evaporation
impurities
exhaust
recycling and treatment

fig. No. 5: Flow scheme of evaporative recovery of chromic acid

Electrolytic Metal Recovery of Copper

The Cu-regenerants and the acid-CU-dragouts are also collected together in a special tank. The solution is used in a chemical process to generate 100 gals per week of an electrolyte with a Cu-concentration of about 15 oz/gal. Then, the electrolyte is pumped into a specially designed electrolytic metal recovery unit (see fig. No. 6) and in about 3 days, 100 lbs of copper are plated out as metal sheets. The efficiency of this process is 98%.

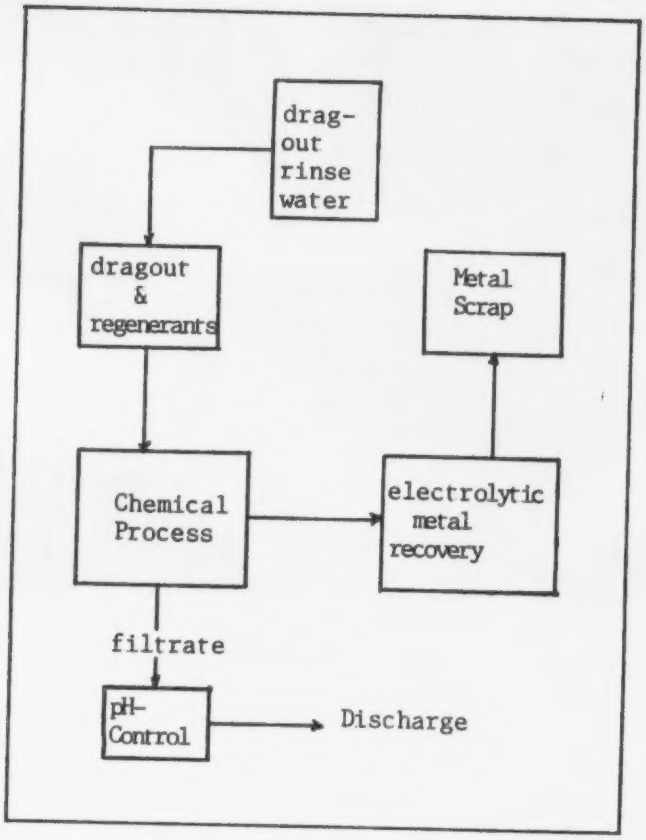
drag-
out
rinse
water
dragout
&
regenerants
Metal
Scrap
Chemical
Process
electrolytic
metal
recovery
filtrate
pH-
Control
Discharge

fig. No. 6: Flow scheme of the copper recycling

The copper sheets can be easily peeled off the electrodes (see fig. No. 7) and have a metal content of 99.95% of copper which can be sold to a refinery.

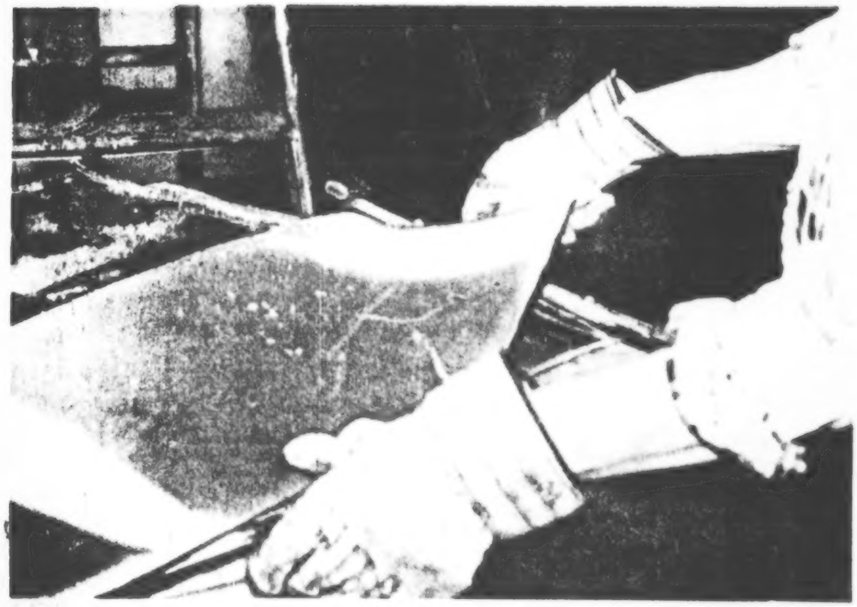

fig. No. 7: Taking metal off electrode

Nickel recycling

The Nickel-regenerants and the Nickel-dragout are pumped into a neutralization or batch treatment tank to precipitate the metal. The Nickel-precipitants are then separated from the liquid in a filter press and rinsed properly.

The next step is a dissolving process to generate a Nickel-Sulfate solution. Eighty gals per week of this Nickel-solution with a Nickel-Sulfate content of about 30 to 35 oz/gal are used for the makeup of the plating baths. A flow scheme of this process is shown in fig. No. 8.

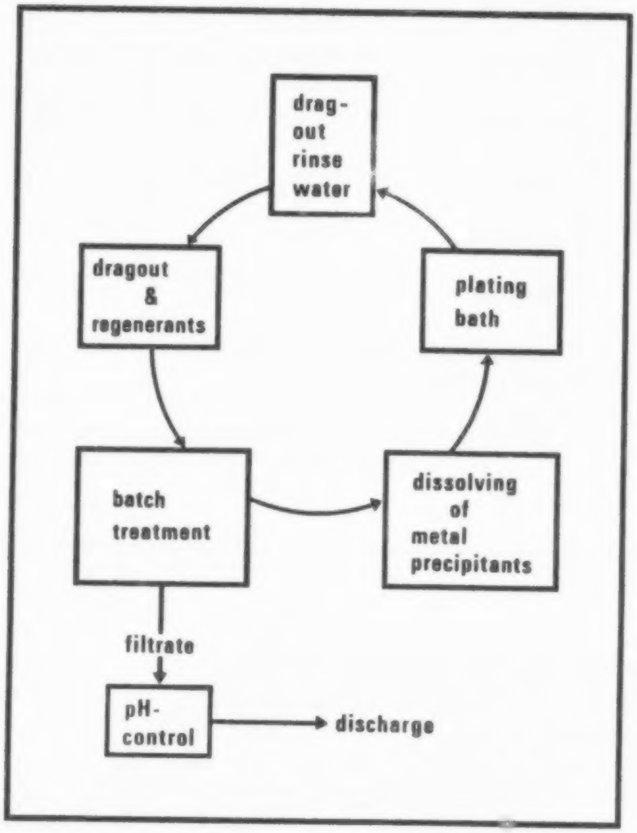
drag-
out
rinse
water
dragout
&
regenerants
plating
bath
batch
treatment
dissolving
of
metal
precipitants
filtrate
pH-
control
discharge

fig. No. 8: Flow scheme of a Nickel recycling process

Ecological and Economical evaluation

A three day monitoring and sampling of the discharge of the plating plant demonstrated that the company is in compliance. Table No. 2 and fig. No. 9 show the discharge data before and after setting up the recycling system.

	Before	After
CHROME	37.00	1.16
COPPER	14.40	0.48
NICKEL	19.33	1.30
ZINC	0.67	0.17
CYANIDE	7.82	0.40
TOTALS	79.22	3.51
TOTAL DISCHARGE (Gals/Day)	270,000	79,000

Table 2: Data of discharge before and after setting up the recycling system.

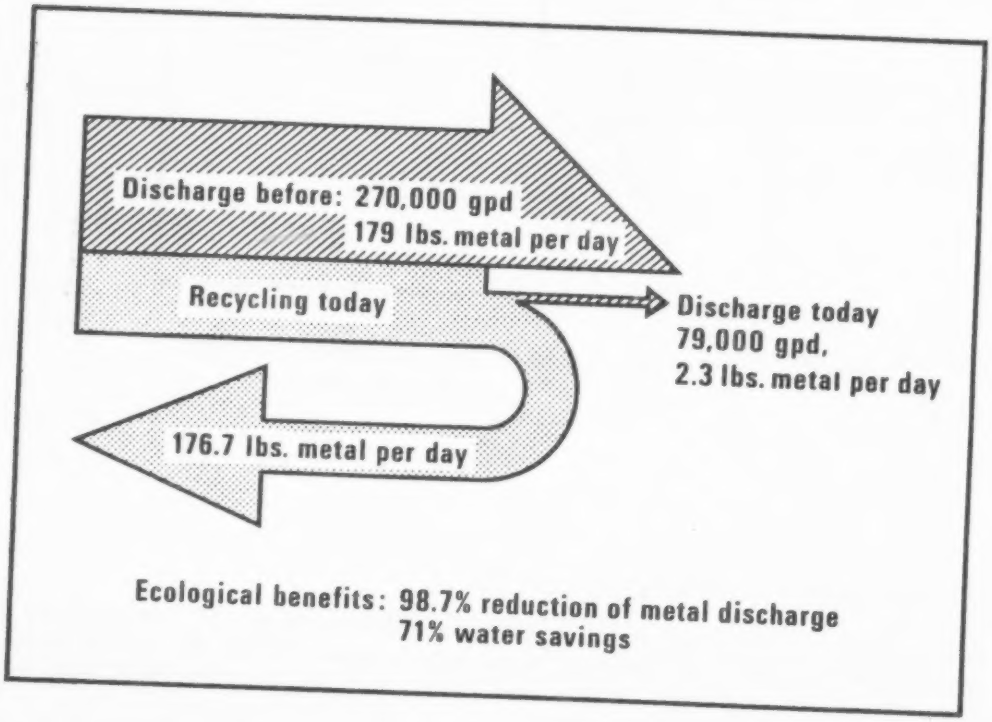
Discharge before: 270,000 gpd
179 lbs. metal per day
Recycling today
Discharge today
79,000 gpd,
2.3 lbs. metal per day
176.7 lbs. metal per day
Ecological benefits: 98.7% reduction of metal discharge
71% water savings

fig. No. 9: Ecological benefits of the system

The operation of the recycling system reduced metal discharge by 98.7% and used 71% less water. It should be pointed out that the discharge shown in table No. 2 is untreated waste water. The rinses behind cleaners, activators, acids, etc., can be discharged directly because their metal content is extremely low. This means that in this case only, the rinse systems behind every plating bath were the sources of pollution. Through installation of the ion exchange columns, the pollution source is eliminated.

In accordance with the described recycling operations, the economical benefits stated in weekly figures are as follows:

SAVINGS PER WEEK	
MATERIAL	AMOUNT
WATER	955,000 gallons
NICKEL SULFATE	80 gallons
CHROMIC ACID	200 lbs.
SOLID COPPER SCRAP	100 lbs.

A further benefit is that no sludge is created. If this facility would operate a conventional waste water treatment system, approximately two tons of hazardous waste would be generated.

This is a critical environmental factor which further emphasizes the absolute importance of recycling rather than continuing wasteful habits.

A first analysis of the recycling system shows that savings exceeded operating costs.

References:

1. F. Reinhard, "Rinse Water Treatment and Metal Recycling in Plating Shops", Galvanotechnik 73, 10 (1982) 1089.

2. F. Reinhard, "Pilot System for the Recycling of Heavy Metals in the Electroplating Industry," report at the "International Recycling Congress" in Berlin, 4-19-82.

3. F. Reinhard, "RMA-Closed Loop Waste Water Treatment and Recycling System", 72nd Annual Technical Conference Proceedings of the AES, SUR/FIN 1985.

FINDING A SAFE ECONOMICAL METHOD FOR METAL-FINISHING SLUDGE DISPOSAL

Cynthia Harvey Draper and Raymond W. Regan
The Pennsylvania State University

Abstract

As metal finishers undoubtedly know, disposing of hazardous and toxic metal-finishing sludge (MFS) in a manner acceptable to the EPA and state regulatory agencies is both costly and difficult. One reason for this difficulty is that the number of EPA and state-approved secure landfills which will accept MFS is decreasing.

A more economical and environmentally safe method of MFS disposal is needed to resolve this dilemma. But what can the metal-finishing industry, government regulators, and university researchers do to find better disposal methods? The purpose of this presentation is to propose an answer to this question and to describe work conducted at The Pennsylvania State University. A proposal is then made to industry to support a field scale demonstration of the concept.

The research involved the examination of a specially designed monofill concept, as proposed by Lancy.[1] Laboratory experiments were performed using model reactors containing a layer of calcinated lime pellets to simulate the precipitation and removal of heavy metals (Cd, Cr, Cu, Ni, Pb, Zn) from prepared solutions of MFS leachate. Residual soluble metal concentrations were determined to be generally at or below that predicted by equilibrium chemistry theory, 0.005 to 0.15 mg/ℓ.

A field scale demonstration study by the Penn State researchers, in cooperation with Lancy International, Inc. (Zelienople, Pa.) is proposed to examine the environmental effects, economics and metal reclamation potential for a small regional MFS monofill.

Introduction

In order to address the needs of the electroplating/metal finishing industry in Pennsylvania, the Office of Hazardous and Toxic Waste Management (OHTWM) at The Pennsylvania State University contracted with Dr. L. E. Lancy (Lancy International, Inc., Zelienople, Pa.) to prepare a report on the state-of-the-art technologies used to treat metal finishing solid and liquid wastes.[1] The report examined the various waste control options available to both job shops and captive facilities in Pennsylvania noting critical concerns for small urban job shops. The needs and solution approaches recommended in the report have application to a large number of similar facilities around the country.

The general purposes of this paper are to summarize Lancy's concept for MFS disposal and to describe an experimental program conducted by OHTWM to expand the data base needed for developing design criteria for a land based treatment and disposal method suitable for MFS. As proposed by Lancy, this approach may offer an economical alternative to conventional MFS disposal in secure, EPA approved landfills.

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Chemical Characterization of Wastewater

The chemical species in the wastewater varies for each metal plated, including acids, cleaning agents and residual solubilized metals (Table 1).

Table 1. Concentrations of Acids and Temperatures Used at One Plating Plant.[2]

	Acid pickle A & B[a]	Acid dip D	Acid etch C	Nitric dip F	Bright dip P
Basis metal	Steel	Aluminum	Various	Aluminum	Zinc
Hydrogen chloride conc., %	17	0	0	0	0
Hydrogen fluoride conc., %	0	13	--	0	0
Nitric acid conc., %	0	43	0	50	1
Sulfuric acid conc., %	0	22	28	0	0
Temperature, °C(°F)	24(75)	24(75)	21(70)	24(75)	24(75)

[a] A & B were separate tanks sampled at the same time.

Sodium cyanide, is used to clean metal surfaces and is common to many plating operations. For instance, a bath containing NaCN was used to preclean steel to be plated with nickel.[3] Obviously, the wastewater would also contain the metal(s) being plated. Cadmium, lead, chromium, nickel, zinc, manganese, copper, silver, and gold were present in the wastewater of 12 metal-finishing plants surveyed.[4] Chromium was the most common metal in the 12 wastewaters.

Precipitation is considered a well established, reliable method for the removal of metals from wastewater[5] and is widely used by the existing job shops to meet EPA-wastewater effluent guidelines.[7]

Solid Waste Quantities

Generally, the MFS generated from electroplating operations constitute the major hazardous solid waste disposal problem for the industry.[1] Quantities of hazardous wastes generated by selected Pennsylvania firms classified as electroplaters and metal finishers were complied based on manifest documents received by the Pennsylvania Department of Environmental Resources (PaDER) (Tables 2 and 3). The waste generation data indicate several salient features of the industry, namely, (1) many electroplating operations (SIC 3471) produce HW other than MFS (F-006) and MFS generated

Table 2. Quantities of Hazardous Waste Generated by Selected Pennsylvania Electroplaters During 1981[a].

Firm	Waste Codes[b]	Shipments	Tonnes
A	D-002	3	4.55
	D-007	1	4.50
	D-000, D002	2	1.35
B	D-002	1	0.25
	F-002	1	0.25
	F-017	2	12.71
	D-002, F-018		40.30
C	F-001	6	4.50
	F-006	1	17.82
D	F-002	1	1.05[d]
	F-006		38.0[d]
E	F-006	1	14.24
F	F-007	1	0.63

NOTES: [a] SIC 3471
[b] As defined by the U.S. EPA Hazardous Waste Lists.
[c] Generator producing ≥ 1000 kg/month.

[d] Tonnes = Gallons *0.0038

Table 3. Quantities of Hazardous Waste Generated by Selected Pennsylvania Metal Finishers[c] During 1981[a].

Firm	Waste Codes[b]	Shipments	Tonnes
H	F-006	33	396
I	F-006	12	224
J	F-006	19	267
	F-006, K061	1	10.3
K	F-006, D-006, D-008	41	770

NOTES: [a] SIC 3312, 3313, 3399
[b] As defined by the U.S. EPA Hazardous Waste Lists.
[c] Generator producing ≥ 1000 kg/month.

by the typical firm was much less than the amount by a metal finishing operation within the primary metal sector (SIC 3312, 3313 and 3399); and (2) firms in both groups producing less than 1000 kg/month (circa 1981); were not required to manifest HW shipments and therefore the reported information may not be completely reflective of the HW generation by many small plating operations.

The most recent information available from the PaDER indicates the total MFS generation in Pennsylvania for 1982 and 1983 was 18,622 and 27,311 tonnes per year, respectively.[6]

MFS Leachability

The American Society for Testing and Materials (ASTM) leaching test is an extraction procedure used to predict the leachability of a potentially hazardous sludge into deionized water. Lancy modified the ASTM method by washing out the interstitial water in a MFS before the extraction procedure was performed.[8] In Lancy's opinion, the interstitial water should be removed because it does not have any bearing on the long-term leachability of a MFS. The modified test results indicated that only low and environmentally safe heavy metal concentrations would be leached if the interstitial water were removed. Lancy designed a monofill facility in Maysville, Kentucky using limestone layers placed between layers of MFS. The purpose of the limestone was to provide support for equipment operating on the fill. The data collected from monitoring wells indicated heavy metal concentrations did not exceed the limits set by EPA and Kentucky regulatory authorities, for MFS to be classified as a hazardous waste on the basis of toxicity (Appendix A).

The Penn State Research

We theorized that the heavy metal concentration in the interstitial water of a MFS as reported by Lancy[1] have been neutralized and precipitated by the limestone and trapped in the soil at the base of the monofill to achieve reduced heavy metal concentrations.

In order to examine this concept, two phases of laboratory experiments were conducted. Based on its improved reactivity calcinated lime (CaO) pellets (1/4 to 1/2 inches) was used instead of the limestone ($CaCO_3$). The purpose of the first phase was to estimate the amount of lime needed to react with the soluble metals in the interstitial water of MFS and also to determine how long the soluble metals in the leachate must be in contact with lime in order to form an insoluble metal hydroxide. The purpose of the second phase was to compare the performance of a lime-lined landfill model using normal rain and acid rain conditions, a specific concern for a possible MFS monofill located in Pennsylvania.

Phase I - Experimental Approach

Wastewater effluent from a metal-finishing treatment plant supplemented with desired concentration of heavy metals was used to simulate a "worst case" scenario from a MFS monofill (Table 4).

Table 4. Simulated Leachate Characteristics for Experiments 16, 17, 18 and 19.[b]

Chemical	Soluble concentration[a] mg/ℓ
Cd	0.92
Cr	0.52
Cu	3.77
Pb	0.15, 1.89
Zn	3.22

[a] pH reduced to 5.0 with HNO_3.
[b] Ni, Hg monitored in other experiments.

The leachate was treated by evenly distributing it over a layer of lime in small cylindrical glass reactors 7 cm in diameter and 30 cm in depth. The treated effluent was monitored for pH, and soluble metals. The flow rate and lime depth were varied with each run to estimate the depth of lime and minimum leachate-lime contact time needed for optimum metal removal. Overall, 19 experimental run were conducted.

Phase II

This phase of the study is now in progress and is scheduled to be completed during the Spring, 1986.

In Phase II four landfill models were constructed consisting of four glass cylinders, 5 cm in diameter and 90 cm in depth. The reactors will be operated at the optimum flow rate and lime depth determined from the results obtained in Phase I. Model 1 act as a control and contains no lime layer. Models 2, 3, and 4 contained the desired lime layer beneath the MFS. Model 4 also contained a lime layer above the MFS layer suitable for neutralizing simulated acid rain.

Preliminary Results and Discussion

The results for Phase I are presented only in preliminary data form since the experimental work is still in progress. Phase II experiments are the objective of ongoing studies. Our purpose for this presentation is to highlight selected experimental findings and to briefly discuss the engineering application of these results to a MFS monofill. A more extensive technical presentation will be submitted for publication to Plating and Surface Finishing, Journal of the AES.

Several experiments were conducted to establish a workable combination combination of lime bed depth (2.5 to 20 cm) and contact time. For the experimental reactor used, the combination of a flow of 0.5 to 1.0 mℓ/min when added continuously to a 10 cm deep bed of lime pellets was found to be effective for metal removal. The combination of two factors may be involved namely, the contact time of the leachate with the lime needed to precipitate metal hydroxides and the shear force caused by the leachate flow needed to remove the metal hydroxide from the pellet surface, thereby renewing the surface for further precipitation.

Experiment 17 reactors operated at optimum flow contact time conditions were continued for an extended time to indicate the exhaustion capability of the lime bed (Figures 1A and 1B). Bed exhaustion was indicated by the elevation of the soluble metal concentration (with decrease in pH) to 10 percent of the HW toxicity limit established by EPA. Cadmium was found to be the controlling metal, reaching 0.1 mg/ℓ after approximately 500 hours of reactor operation.

The experimental results indicate decreased soluble metal concentrations for all metals examined except for Cr and Cu near a pH of 7.4 at the very early stages of the run (Figures 2 through 6). Since equilibrium chemistry does not account for the very low soluble metal concentrations at the observed pH levels, adsorption and/or coprecipitation must be responsible. Coprecipitation is the precipitation of a metal below predicted equilibrium solubility limits due to the presence of another metal. The mechanism for coprecipitation is not well understood, but its occurrence is well documented in the literature. The results of Experiments 18 and 19 show that Cr was necessary for coprecipitation to occur from the simulated MFS leachate.

Finally, with the appropriate lime bed depth and leachate contact time, interstitial water present in 100 gm of MFS (at 20 percent moisture) could be treated by 1 gm of lime pellets.

The Next Step

If disposing of MFS in lime-lined monofills is proved to be environmentally safe one might think that the next step would be for the industry to start using the method. Unfortunately, laboratory studies may prove the concept, but do not offer sufficient information to justify a cost-effective application. A demonstration study is proposed by OHTWM, in cooperation with Lancy International to examine the environmental effects and cost-effectiveness of a regional, MFS monofill to be operated as a final disposal area, with a possible option for metal reclamation of appropriate MFS. A successful demonstration should provide the information needed by regulatory authorities and the industry to establish the method's safety and economic benefits.

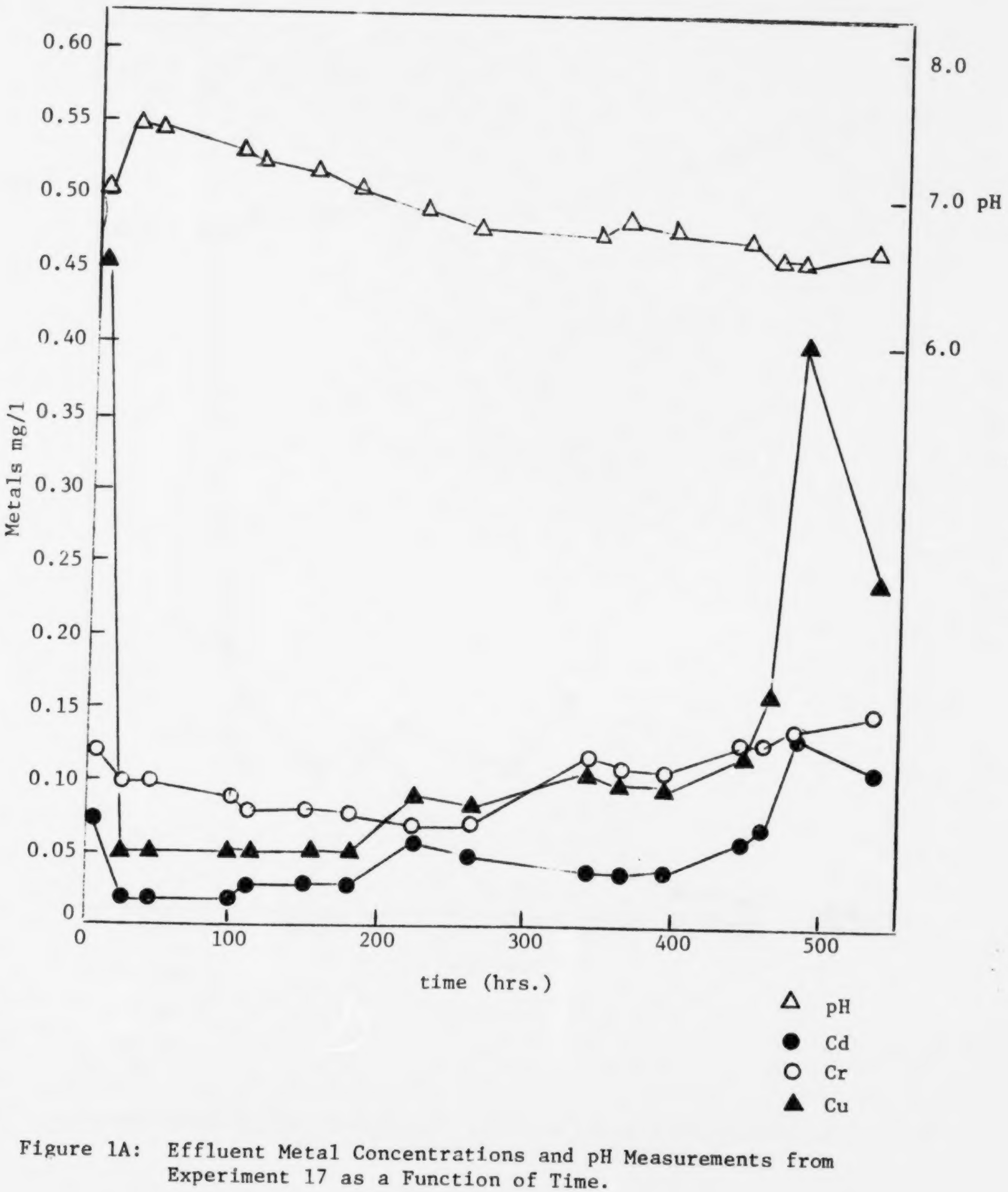

Figure 1A: Effluent Metal Concentrations and pH Measurements from Experiment 17 as a Function of Time.

Q7

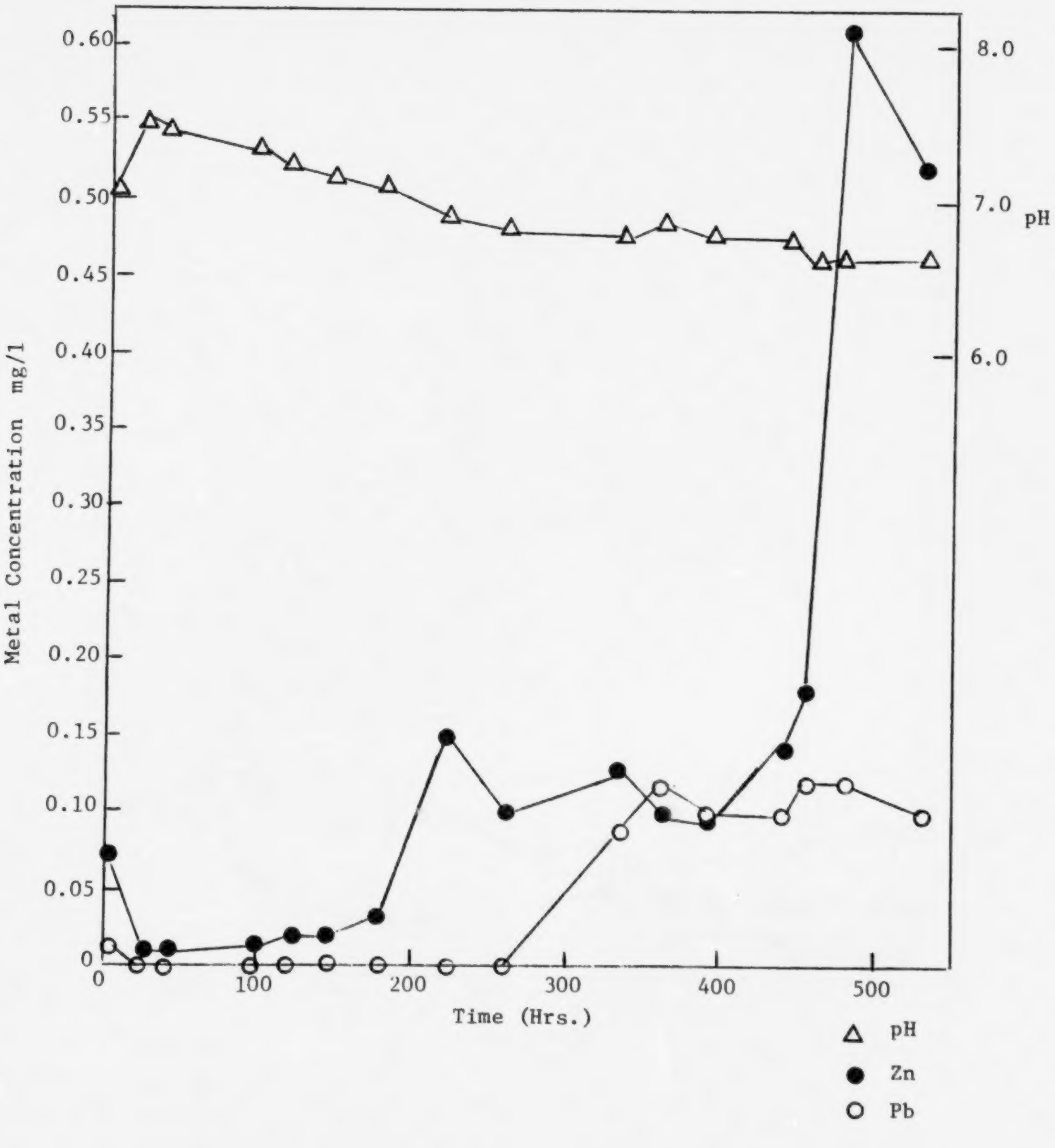

Figure 1B. Preliminary Data; Metal Concentrations and pH Measurements from Experiment 17 as a Function of Time.

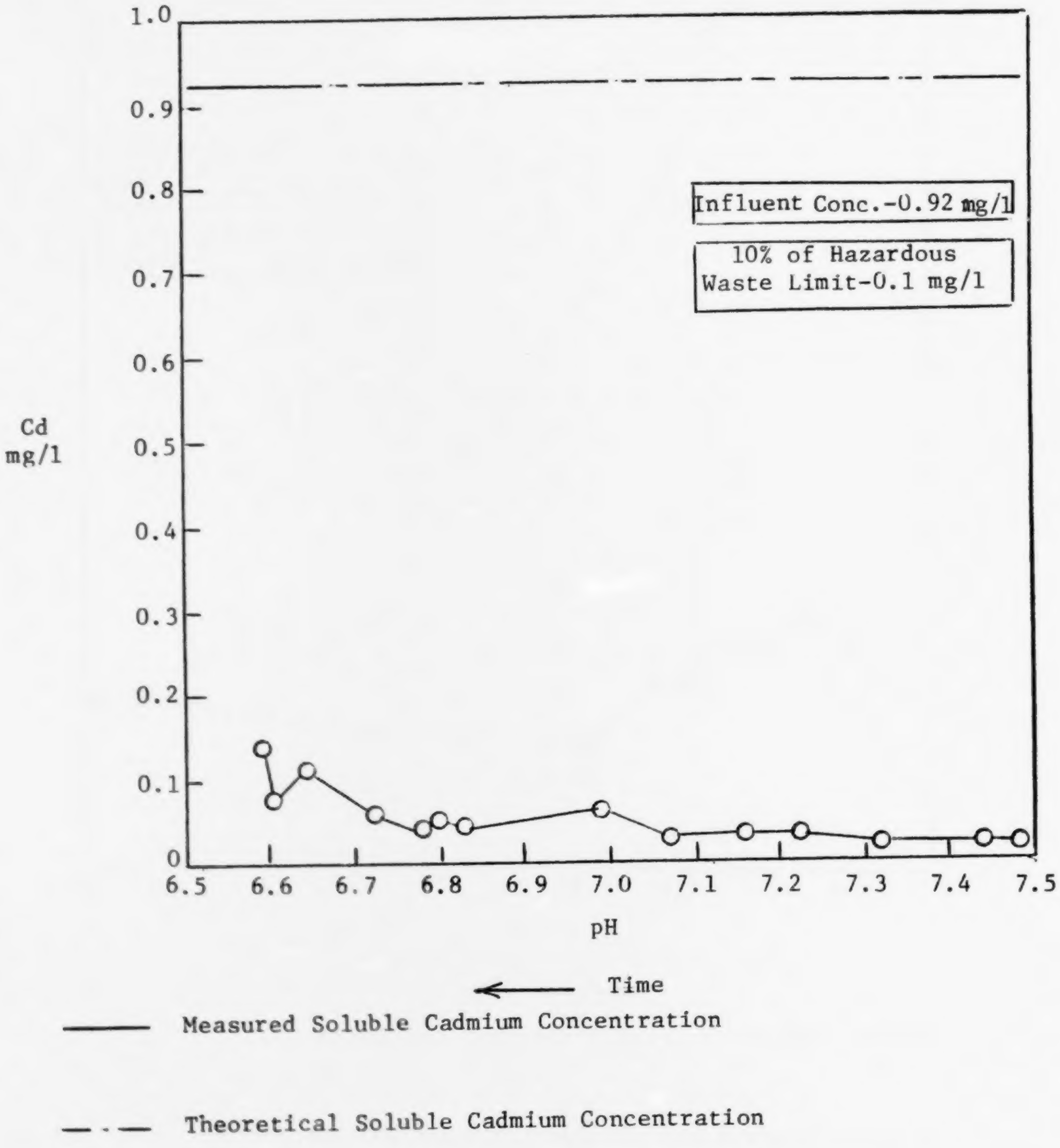

Figure 2: Preliminary Data; Theoretical and Experimental Soluble Cadmium Concentration as a Function of pH.

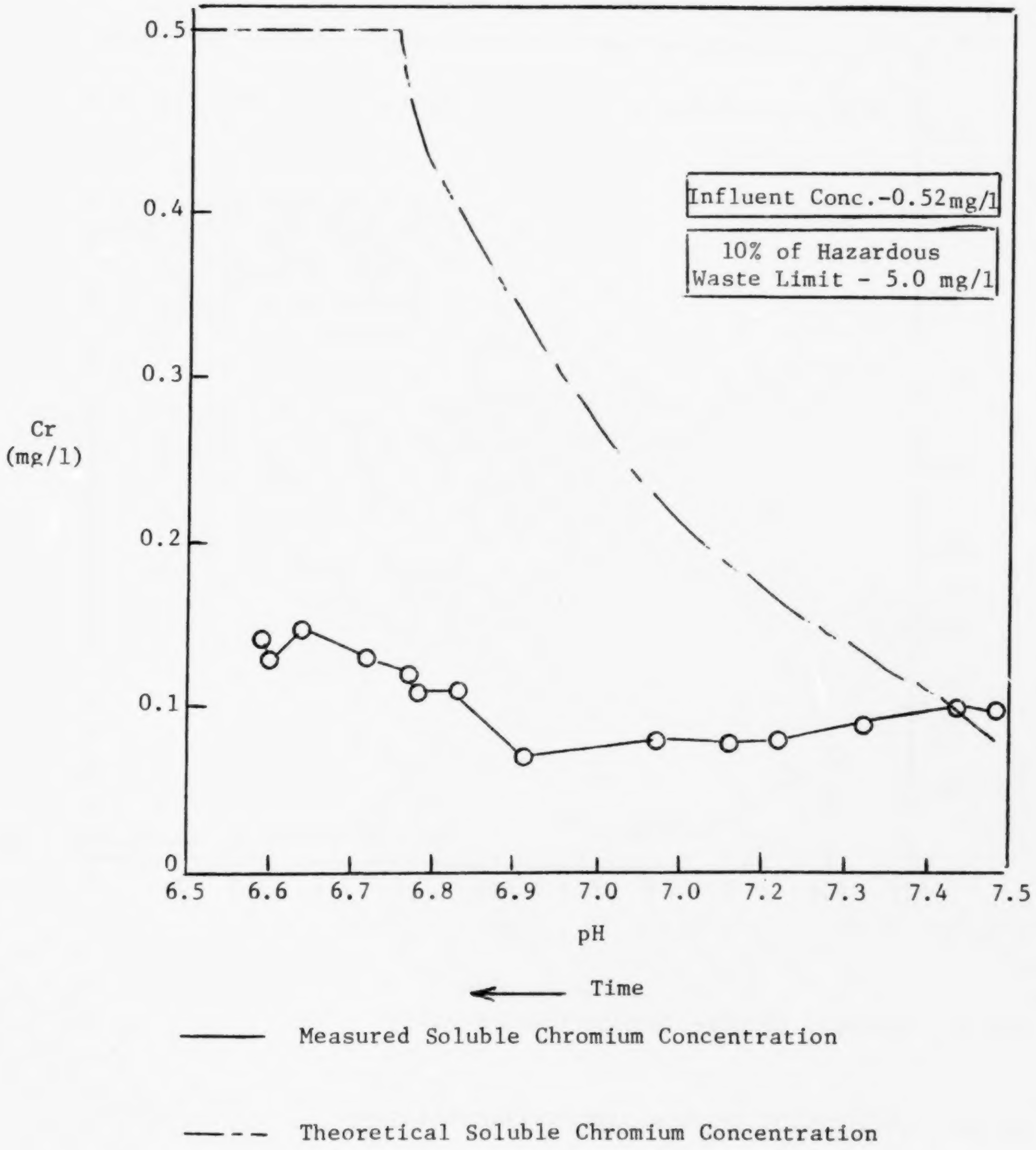

Figure 3. Preliminary Data;Theoretical and Experiment Soluble Chromium Concentration as a Function of pH.

Q10

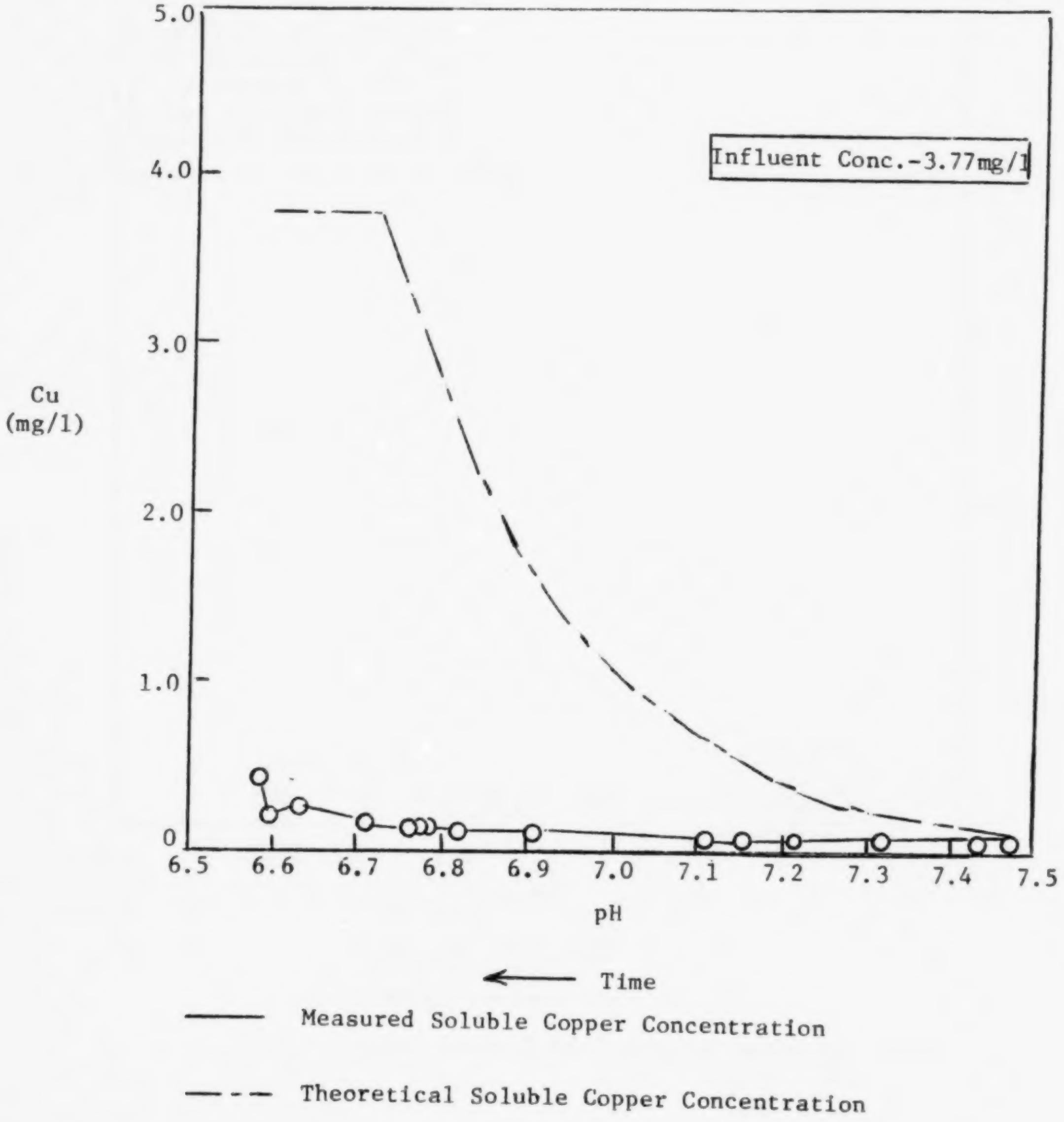

Figure 4. Preliminary Data; Theoretical and Experimental Soluble Copper Concentration as a Function of pH.

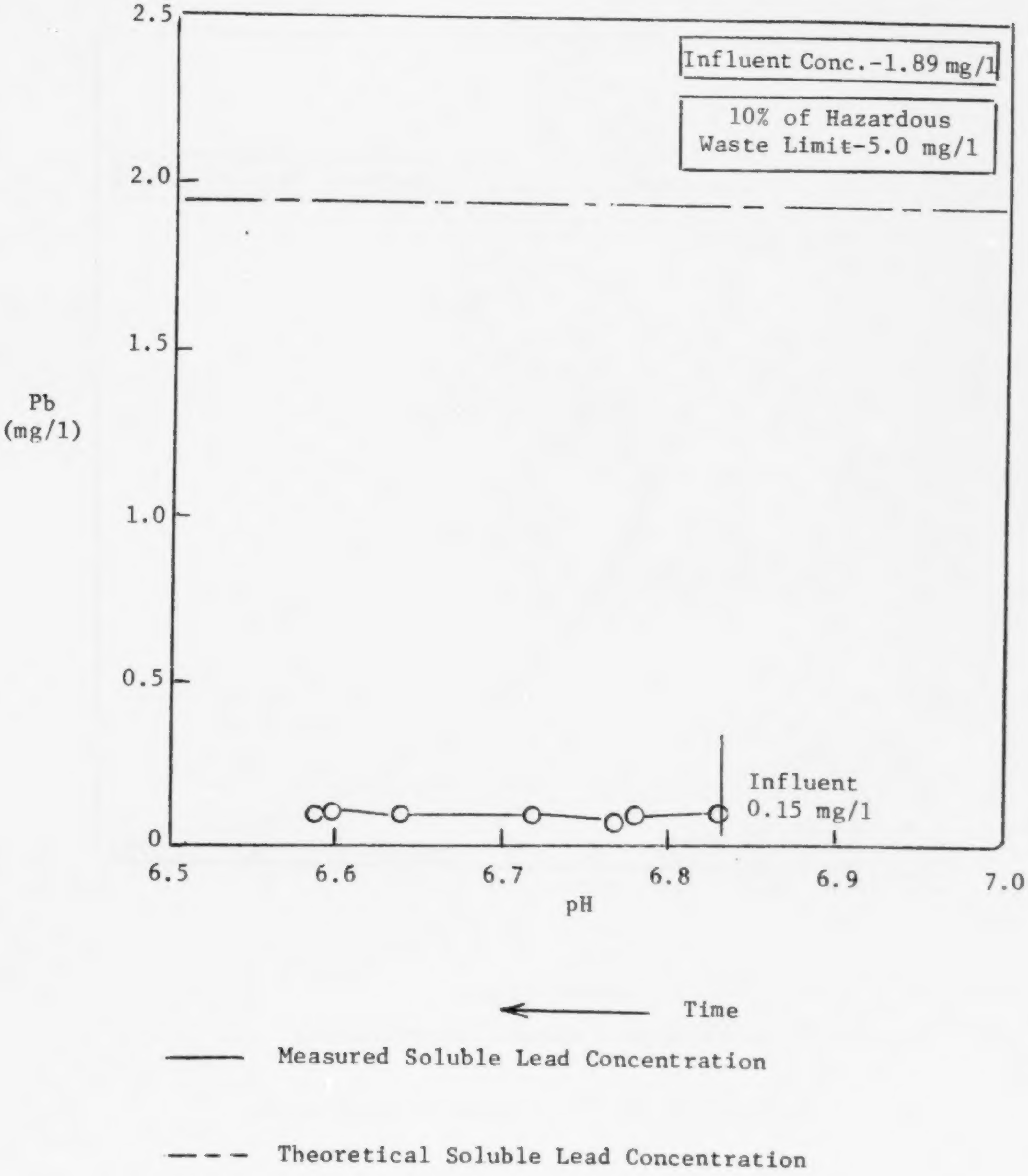

Figure 5. Preliminary Data; Theoretical and Experimental Soluble Lead Concentration as a Function of pH.

Q12

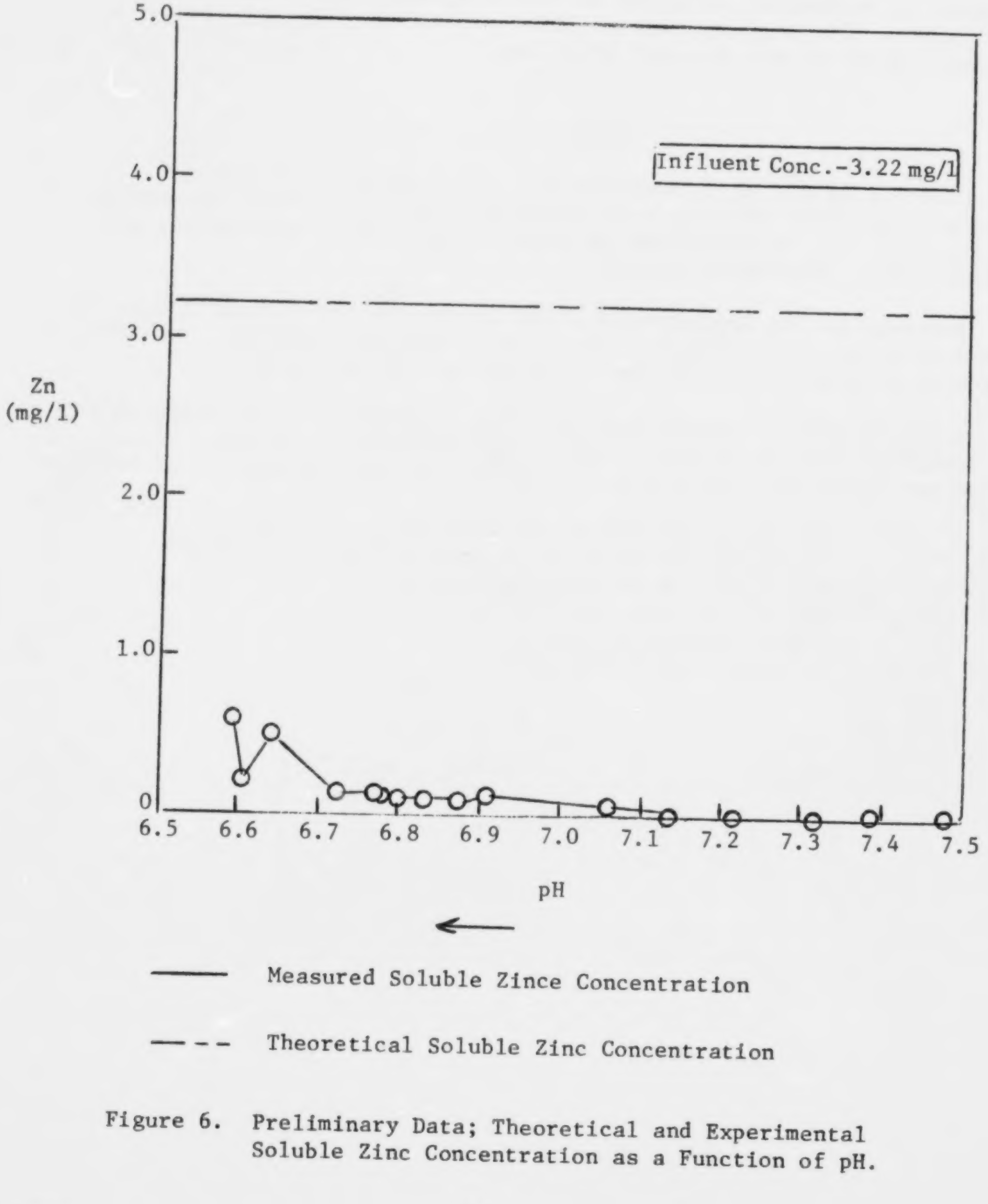

Figure 6. Preliminary Data; Theoretical and Experimental Soluble Zinc Concentration as a Function of pH.

What part can metal finishers and government officials play? The research described here, and the proposed demonstration study, needs the support of both the metal-finishing industry and government officials. The proposed demonstration study will require a financial commitment from participating metal finishers and approval from regulatory agencies. If EPA, state regulatory agencies, and the metal-finishers cooperate on this research, an economical solution for MFS disposal could be achieved in the near future. The proposed demonstration project is intended to have a national impact on MFS disposal practices.

Conclusion

Landfilling MFS as a hazardous and toxic waste is costly, and government-approved landfills are often difficult to locate. Something must be done, but no action can be taken without first identifying and testing better processing methods.

Research at The Pennsylvania State University has already begun, but your cooperation is needed in order to continue the research. Together, a more cost-effective solution for MFS disposal can be found.

We would greatly appreciate your timely comments on our research and its potential benefit to you. Small firms located in the Mid-Atlantic region are especially requested to respond. You may contact us as follows:

Office of Hazardous and Toxic Waste Management
Institute for Research on Land and Water Resources
The Pennsylvania State University
University Park, PA 16802
Attn: Raymond W. Regan
or call: (814) 863-1518

Acknowledgment

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References

1. Lancy Laboratories Division, Lancy International, Inc., "Waste Treatment and Hazardous Waste Management Problems Facing the Metal Finishing Industry in Pennsylvania," prepared for Office of Hazardous and Toxic Waste Management, Institute for Research on Land and Water Resources, The Pennsylvania State University, LW8407, (1984), 47 pp.

2. "Control of Workplace Hazards in Chromium Plating and Acid Cleaning Operations," Plating and Surface Finishing, (January, 1985).

3. Strauss, Randy. "Preplate Preparation for Electroless Nickel Plating," Plating and Surface Finishing, (January, 1985).

4. Meredith, J. W. "Electroplating Wastewater Sludge Characterization," EPA-NTS 600/Z-81-064, (July, 1980).

5. Kovalcik, Robert. "Removing Heavy Metals from Printed Circuit Wastewater, Plating and Surface Finishing, February, 1985.

6. Popovich, Paul. PaDER, Solid Waste Management Information System, Pa. Quarterly Report/Interstate Manifest, Hazardous Waste Year-to-Date Summary for 1982 and 1983.

7. "Environmental Pollution Control Alternatives: Economics of Wastewater Treatment Alternatives for the Electroplating Industry," EPA 625/5-79-016, 1979.

8. Penland, J. L., F. A. Steward and L. E. Lancy. "Modified Leach Test Incorporating and Elutriation Step for the Evaluation of Metal Sludges" in ASTM Special Technical Publication 760, ASTM, Philadelphia, PA, (1981), pp. 186-200.

APPENDIX A

Leachate Concentrations Monitored at the Maysville, Kentucky MFS Monofill (Reference 1, p. 35)

CONCENTRATION (mg/l)

Leachate	PH	CN	Cr^{6+}	Cr^{3+}	Zn	Ni
EPA Standard		+	5	5	+	+
Date						
8/12/74	7.75	*	*	0.03	0.14	0.09
12/4/74	8.0	*	*	*	0.02	0.10
4/24/75	8.1	*	*	*	0.01	0.02
5/28/75	7.45	*	0.09	*	*	0.10
8/8/75	8.45	*	0.70	*	0.06	0.39
12/2/75	7.7	0.06	0.14	0.03	0.10	1.21
4/2/76	8.85	0.01	*	*	0.04	3.18
8/10/76	7.40	*	*	*	0.02	0.01
12/28/76	7.20	*	*	0.05	0.07	0.01
4/12/77	7.15	*	*	0.17	0.07	0.19
8/11/77	7.25	0.03	*	0.12	0.28	0.05
12/14/77	7.15	*	*	0.13	0.41	0.05
4/20/78	7.75	*	*	0.03	0.08	0.12
8/1/78	7.25	*	*	0.08	0.01	0.15
3/2/79	7.35	*	*	*	0.03	*
4/24/79	7.65	*	*	*	0.02	*
8/15/79	9.35	0.05	0.05	0.46	0.01	0.15
1/9/80	7.40	*	*	0.06	0.17	0.06
4/2/80	7.15	*	*	0.16	0.02	*
6/27/80	7.30	0.02	*	*	0.07	0.20
9/22/80	7.20	*	*	0.05	0.02	0.04
12/1/80	7.25	*	*	0.41	0.06	0.04
3/6/81	7.35	*	*	*	0.04	*
8/11/81	7.10	*	*	0.04	0.02	*
1/4/82	8.2	*	*	0.07	0.15	0.04
4/1/82	7.8	*	*	*	0.02	*
8/10/82	8.2	0.01	*	0.05	0.12	0.34
12/21/82	7.3	*	0.01	0.01	0.08	0.08
4/12/83	8.2	*	*	0.05	0.24	1.21

+ No EPA Standard
* Less than 0.01 mg/l

MAGNESIUM HYDROXIDE
A UNIQUE NEUTRALIZER FOR REDUCING SLUDGE VOLUMES AND IMPROVING FILTERABILITY

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INTRODUCTION

Magnesium hydroxide is an alkali that has been used for many years to neutralize acid. The medicinal neutralization which many people are familiar with is neutralization of stomach acids using "milk of magnesia", in which the major ingredient is magnesium hydroxide.

In wastewater management, one common and cost effective way to treat acid waste streams containing dissolved metals is through chemical precipitation of the metal hydroxide with alkalies such as caustic (NaOH), lime (CaO) and soda ash (Na_2CO_3). Magnesium hydroxide [$Mg(OH)_2$] has been found-to be effective in neutralizing acids, as well as removing unwanted metal contaminants in electroplating and metal finishing wastewaters. Magnesium hydroxide does not act nor react like conventional alkalies, and it is the intent of this presentation to provide a better understanding of the unique characteristics of this alkali and how to incorporate it into a treatment facility to produce a lower volume, more dense metal hydroxide sludge that is easier to dewater.

PROPERTIES

Magnesium hydroxide is available as an aqueous white slurry [55-60% $Mg(OH)_2$] of agglomerated particles (particle size distribution 0.6 to 10.0 microns) with a bulk density of 12.5 lbs/gal. This highly viscous (4-40 poise, Brookfield Viscometer #4 Spindle at 20 rpm) thixotropic slurry, which resembles latex paint upon movement, freezes at 32°F and must be kept in mildly agitated storage. The solubility is very low at ambient temperatures (0.0009 g/100 ml H_2O at 18°C) and even lower as the temperature is increased (0.0004 g/100 ml H_2O at 100°C). As mentioned earlier, magnesium hydroxide is comparable to a concentrated milk of magnesia product and, therefore, can be classified as a low-degree health hazard from a handling point of view. Magnesium is one of the most common elements on earth and is an essential nutrient to normal plant, animal and human growth. This, in conjunction with magnesium hydroxide's low solubility, would cause a minimal environmental impact in the event of an accidental spill.

When comparing physical and chemical properties of magnesium hydroxide with conventional alkalies (hydrated lime and caustic), several distinct advantages can be noted as shown in Table 1. The first is percent hydroxide (that portion of the chemical which actually neutralizes the acid and precipitates the metals), which is 27% greater for magnesium hydroxide as compared to the hydrated lime and 37% greater than the caustic. This means that fewer pounds of magnesium hydroxide is required to neutralize the same amount of acid;

thus, a reduction in volume of alkali when using magnesium hydroxide.

TABLE 1

COMPARISON OF PHYSICAL AND CHEMICAL PROPERTIES

Property	NaOH	$Ca(OH)_2$	$Mg(OH)_2$
Molecular weight	40.0	74.1	58.3
Percent hydroxide	42.5	45.9	58.3
Heat of solution Kg-Cal/mol	9.94	2.79	0.0
Solubility in water g/100 ml H_2O	42^1	0.185^1	0.0009^2
Reactive pH maximum	14	12.5	9.0
Weight equivalency	1.37	1.27	1
Freeze point °F	61^3	32^4	32^5

1 - 0°C, 2 - 18°C, 3 - 50% solution, 4 - 30% slurry, 5 - 58% slurry

Also, as can be seen in the neutralization of hydrochloric acid (Table 2), since less magnesium hydroxide is required in the neutralization process, there will be a subsequent reduction in the total dissolved salt of the effluent stream. The same scenerio, less magnesium hydroxide and less salt effluent, will occur for the neutralization of sulfuric acid. If hydrated lime is used to neutralize sulfuric acid a precipitate ($CaSO_4$ $2H_2O$) will occur.

TABLE 2

NEUTRALIZATION OF HYDROCHLORIC ACID WITH $MG(OH)_2$ VERSUS NAOH AND $CA(OH)_2$

$Mg(OH)_2$ (79.9 lbs)	+	2 HCl (100 lbs)	---->	$MgCl_2$ (130.5 lbs)	+	2 H_2O (49.3 lbs)
2 NaOH (109.6 lbs)	+	2 HCl (100 lbs)	---->	2 NaCl (160.3 lbs)	+	2 H_2O (36.7 lbs)
$Ca(OH)_2$ (101.5 lbs)	+	2 HCl (100 lbs)	---->	$CaCl_2$ (175.5 lbs)	+	2 H_2O (49.3 lbs)

Another unique characteristic of magnesium hydroxide, as compared to hydrated lime and caustic, is the reactive pH maximum. Excess addition of lime or caustic will cause the pH of waste streams to go to 12.5 and 14.0, respectively. The pH of a magnesium hydroxide slurry is 10.5, but when used to neutralize acidic streams containing diverse ions, it can only obtain a maximum pH of 9.0. This phenomenon is known as a common ion effect (buffering) and is of benefit in the event of operational over-addition. This buffering effect of the pH at 9.0, which happens to coincide with the upper pH limit under the Clean Water Act of 1976, will also be beneficial to prevent resolubilization of some of those heavy metals (precipitate) that you are in effect trying to remove. Metal hydroxides precipitate at various pH levels depending upon the type of metal. In looking at graphical representations of equilibrium data for various concentrations of metal hydroxides versus pH, it can be noted that several metals such as chrome, copper, zinc and lead, to name a few, will become more insoluble as the pH is

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increased. Then a minimum solubility point or pH is reached after which, upon the further addition of hydroxide ion to the media, the insoluble metal hydroxide will become more soluble via complex formation.

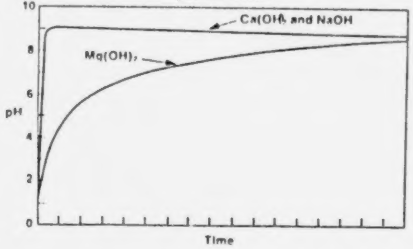
The buffering effect of the pH at 9.0 can also be beneficial for disposing of alkaline wastes downstream of the neutralization without concern for exceeding maximum pH limits of the effluent. Although magnesium hydroxide will begin to precipitate out beyond a pH of 9.0, a considerable amount of alkalinity is required to do this.

A final advantage of magnesium hydroxide, as compared to hydrate lime or caustic, can be noted from a safety point of view. With hydrated lime and caustic, heat will be liberated in the presence of additional water which can be a safety hazard, as well as the fact that they are strong alkalies (bases) which cause severe irritation or burns with eye or skin contact. Magnesium hydroxide is not exothermic and is classified as a weak base and is, therefore, a safe product to handle.

REACTIVITY

As mentioned earlier, magnesium hydroxide does not react like conventional alkalies as seen in Figure 1.

Figure 1
RATES OF ACID NEUTRALIZATION
pH VS TIME



Acid neutralization reactions with hydrated lime or caustic may be considered one-step reactions in which either alkali dissociate immediately to provide hydroxyl ions and a rapid increase in pH. With magnesium hydroxide you have competing reactions occuring, which may be considered a two-step reaction. Magnesium hydroxide, being sparingly soluble, is in equilibrium with the water to produce a limited amount of magnesium and hydroxyl ions. These hydroxyl ions must be consumed by the acid before more magnesium hydroxide particles dissolve to provide additional hydroxyl ion. As more of the acid is being neutralized and the pH increases, less hydroxyl ion is being consumed and the reaction rate slows. The rate of neutralization for magnesium hydroxide is dependent upon various conditions, beside the usual kinetic effects from increased temperature and agitation. One factor that affects the rate of neutralization is the quantity of alkali that is added. By increasing the amount of alkali beyond what is necessary for 100% neutralization, the reaction rate will also increase, but because of its buffering capability, will never go beyond a pH of 9.0. Another factor affecting the rate of neutralization is the level of acid being neutralized. As shown in Figure 2, with a 5% sulfuric acid solution, a pH of 7 is reached in about

Figure 2
NEUTRALIZATION OF VARIOUS CONCENTRATIONS OF H_2SO_4
pH vs TIME
(Based on 105% neutralization)

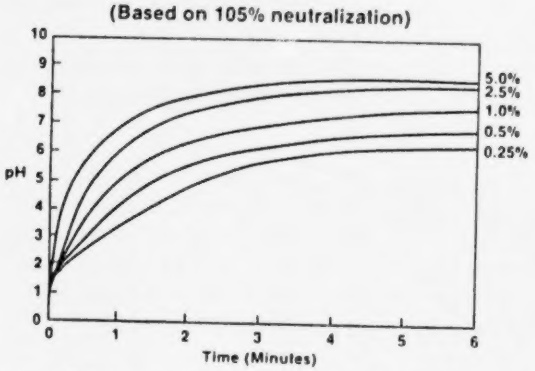
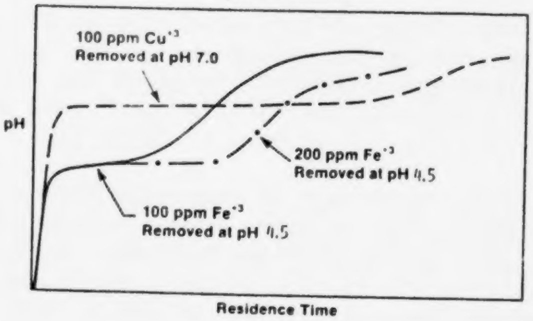


Figure 3
pH vs TIME



one minute compared to ten minutes needed to obtain the same pH when treating 0.25% sulfuric acid. Other factors that affect the reaction rate of magnesium hydroxide are the type and concentration of metal to be removed. As can be seen in Figure 3, the residence time required to remove 100 ppm ferric iron is much less than removal of 200 ppm of ferric iron, and is also faster than the removal of 100 ppm copper.

Often a waste stream will contain a multitude of metals that need to be removed. In using magnesium hydroxide the pH will increase until the level at which the metal to be precipitated is reached. It will remain at that pH until the metal is removed and then will proceed upward. In other words, if a system contained both ferric iron and copper, the pH would rise to 4.5 where ferric hydroxide is precipitated and remain there until all of the ferric iron has been removed. The pH would then rise up to 7.0 where the onset of copper hydroxide precipitation begins.

There are two other reactive characteristics that need to be mentioned. Magnesium hydroxide not only provides hydroxyl ion for metal removal, but can remove metals through surface adsorption. It has been observed that metals can be removed from waste streams despite the lack of an acceptable pH level. Table 3 is an example of such a phenomena:

TABLE 3

SURFACE ADSORPTION

Alkali	pH	ppm Cu
None	1.5	500
NaOH	6.9	3.6
$Mg(OH)_2$	5.6	17.0
$Mg(OH)_2$	9.4	0.2
NaOH	9.3	0.4
NaOH	10.3	0.3
NaOH	10.9	0.5

The first item to note is the magnesium hydroxide at a pH of 5.6. At this pH the copper concentration should be above 100 ppm according to most concentration versus pH profiles. Secondly, the magnesium hydroxide was just as effective in lowering the copper to an equivalent level at approximately 1 pH unit less than the caustic; i.e., pH 8.4 - 0.2 ppm Cu vs pH 9.3 - 0.4 ppm Cu). Finally, it can be seen that as you increase the pH of the caustic from 10.3 to 10.9 that the copper begins to resolubilize. Therefore, when using magnesium hydroxide, a change in operating procedures or expectations is necessary.

The second reactive characteristic pertains to flocculant (polymer) addition. Flocculant addition will cause the unreacted magnesium hydroxide particles to coagulate with the sludge and its reaction is terminated.

In summary, there are several factors that can affect the reaction rate of magnesium hydroxide with acidic metal waste streams. It is a culmination of these effects which requires longer residence times for using magnesium hydroxide as compared to hydrated lime and caustic for acid neutralization and metal removal. This additional residence time may appear to be a deterrent for using magnesium hydroxide but is the basis to make it attractive from a sludge production and handling point of view.

SLUDGE CHARACTERISTICS

The type of metal hydroxide precipitate that forms when using hydrated lime and caustic tends to be extremely light and friable. The instantaneous formation/precipitation results in numerous small particles that are interdispersed with water to form a gelatinous type sludge. The type of sludge formed with magnesium hydroxide is more particulate in nature and can be attributed to the longer reaction time which is condusive for crystal growth. The difference in a particulate sludge versus a gelatinous sludge can be seen in Figure 4, which is the result of treating a sulfuric acid waste stream containing 1000 ppm chrome with caustic, hydrated lime and magnesium hydroxide. It is not uncommon to see volume differences of 50% or greater. Not only is the volume reduced with a particulate sludge as compared to a gelatinous sludge, but the density is greater for the particulate as can be seen in the opacity differences at the tips of the volumetric centrifuge tubes. It should be noted that on a dry weight basis, the amount of sludge in the three tubes is approximately the same with the exception of the $CaSO_4$ $2H_2O$ portion of the sludge formed with the hydrated lime. Another difference that is often noted is color variations between the sludges.

One advantage of a particulate sludge is its increased porosity and permeability, which is dramatically observed in its handling and dewatering characteristics.

Table 4 is data based on experience with several chrome plating operations.

TABLE 4

TYPICAL SLUDGE PROPERTIES FROM A PLATE AND FRAME FILTER PRESS

Chemical	% Solids	Sludge Density (Lb/Ft^3)	Filter Press Cycle Times (Hr)	Yd^3 Sludge 10,000 Lbs Solids Generated
NaOH	30	80	7-9	15
$Ca(OH)_2$	35	85	7-9	12.5[1]
$Mg(OH)_2$	55	100-110	1.5-2	6.4

[1] Consists of both metal hydroxide plus $CaSO_4$ $2H_2O$ from sulfuric acid in plating bath.

R5

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It should be noted that not only is there an increase in the percent solids and sludge density using magnesium hydroxide, but the ease with which the dewatering equipment can separate the solids from the liquid (filter press time). These results will vary from time to time, reflecting the change in wastewater due to changes in upstream production process.

How this reduction in sludge and ease of dewatering translates to actual savings is shown in the following example.

Basis:

- 341 M lbs/yr of lime at $98/ton delivered
- 267.5 M lbs/yr of magnesium hydroxide at $274/ton (includes freight to western Pennsylvania)
- 1,238 yd^3/yr of sludge produced by lime
- 206 yd^3/yr of sludge produced by magnesium hydroxide
- $40/yd^3 sludge disposal cost
- Labor manpower cost only

	$ Alkali Cost		$ Sludge Disposal		Labor		Total
$Ca(OH)_2$	16,709	+	49,520	+	15,000	=	81,229
$Mg(OH)_2$	36,648	+	8,240	+	2,000	=	46,888

These cost saving estimates for the use of magnesium hydroxide do not include maintenance costs associated with the scaling effects of lime nor the incremental maintenance costs for additional equipment operation.

Another economic benefit which has been observed in the use of magnesium hydroxide is associated with the reduction in the amount of flocculant (polymer) used for flocculation. Several cases have been noted where flocculant (polymer) usage has been cut in half, and again this can be attributed to the increased density of the sludge and a faster settling rate.

Magnesium hydroxide can be a very cost effective alkali replacement for neutralization of acidic metal waste streams by reducing the volume of sludge that is generated and improving the dewatering characteristics.

OPERATING TECHNIQUES

As indicated earlier, a time requirement is necessary in order for the magnesium hydroxide to produce a particulate sludge. Consequently, it is necessary to address this time requirement and how it can be incorporated into a waste treatment system.

Hydrated lime and caustic are generally added to a waste until a desired pH is reached. This cannot be done with magnesium hydroxide if it is going to be used most efficiently. Rather than adding magnesium hydroxide until a desired pH is reached, one must calculate how much to add beforehand. At first this may seem complicated, but in reality is quite simple. The most straightforward operation is in a batch neutralization system. Generally, 100 ml of sample from the batch tank is taken and titrated with a one normal

(1N) solution of sodium hydroxide to the desired pH. The volume of sodium hydroxide (caustic) used in the titration is then used to determine the amount of 50% caustic required to neutralize that batch by the following calculation:

$$\text{gals } 50\% \text{ NaOH} = \text{gals of waste} \times \text{ml of } 1N \text{ NaOH} \times 0.000523$$

After determining the amount of 50% caustic required to neutralize the batch, multiplication of that amount by 0.65 will provide an equivalent volume of 57.5% magnesium hydroxide that needs to be added. Add that quantity all at once, and wait until the pH reaches the desired level. Experience has shown that the bulk of sludge is formed in the first 20 minutes. Hence, if time is not available for the full reaction, one may "top off" the batch with lime or caustic (typically less than 10% on an alkali basis) to remove the remaining metals immediately. By topping off, one will produce a sludge with characteristics not quite as good as magnesium hydroxide by itself, but will still be better than using conventional alkalies by themselves.

Application of magnesium hydroxide for a continuous neutralization system again appears somewhat complicated, but can be handled with ease once the correct information is obtained beforehand. Like a batch treatment, one must first titrate a 100 ml sample of waste with 1N NaOH to ascertain the amount of alkali to achieve the desired pH. Then add an equivalent amount of magnesium hydroxide, by the following calculation,

$$\text{grams } Mg(OH)_2 = \frac{\text{ml of } 1N \text{ NaOH} \times .03061}{\% \; Mg(OH)_2}$$

to an identical size sample to determine a neutralization rate (pH versus time). This relationship will show an early targeted pH that must be obtained in order to reach the final desired pH. Once the system is in operation, it is often necessary to fine tune the system by adjusting the initial targeted pH up or down to achieve the final desired pH.

In the event that there is not a sufficient amount of residence time, several options can be used:

1. Alkali addition in upstream sumps or collection lines.
2. Partitioning of neutralization tanks or basins to prevent shortcutting.
3. Increase agitation.
4. Incorporate additional tankage.
5. Topping off as mentioned before.

In the use of magnesium hydroxide as an alkali for the neutralization of acid/metal waste streams, it will be necessary to make modifications in waste treatment operating procedures and/or equipment. Based on extensive experience this can easily be incorporated trouble free.

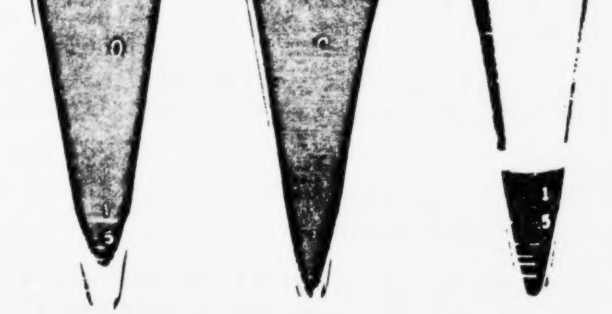
Summary

Magnesium hydroxide has some unusual characteristics which make it cost-effective for neutralization of acidic metal waste streams. Its uniqueness for providing a lower volume of sludge that can be dewatered more easily becomes even more attractive as disposal costs continue to escalate. Because it does not act nor react like conventional alkalies, modifications in waste treatment operating procedures and/or equipment will need to be made. This can often be done quite easily. Reduced maintenance requirements, safety in handling and minimal environmental impact are just a few other value added benefits that can be realized by the use of magnesium hydroxide.

Acknowledgements

The author wishes to express appreciation to the management of Brine Products, Specialty Chemicals and Fabricated Products Department, Dow Chemical, U.S.A. to publish this paper and to my cohorts, Roy A. Davis, and Kathy A. Eickholt for their support. And, special thanks to Sue Schymanski and Nancy Storr for preparing this manuscript for publication.

Figure 4



The one on the left was precipitated by sodium hydroxide. The one in the middle was precipitated by calcium hydroxide, and the one on the right by magnesium hydroxide.

DEVELOPING AND IMPLEMENTING AN EFFECTIVE HAZARD COMMUNICATION PROGRAM

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Introduction

According to a National Occupational Hazards Survey (NOHS) conducted by the National Institute for Occupational Safety and Health (NIOSH) approximately 25 million American workers, or one in four, are potentially exposed to one or more chemical hazards. As many as 40 to 50 million Americans may have been exposed at some point during their lifetimes to one or more of the hazardous chemicals presently regulated by the Occupational Safety and Health Administration (OSHA). OSHA concluded that chemical exposures in the occupational setting and particularly in manufacturing industry, are frequent, and that there was a need for further regulation to help reduce the incidence of both acute and chronic chemically related injury and illness.

On November 25, 1983 OSHA promulgated the "Hazard Communication" Standard, Title 29, Code of Federal Regulations, Part 1910.1200. More than 14 million workers in 300,000 manufacturing establishments will be affected by this new OSHA standard. The purpose of the standard is to establish uniform requirements concerning access to, and dissemination of workplace chemical hazard information. The "Hazard Communication" Standard (HCS) required chemical manufacturers and importers, effective November 25, 1985, to evaluate the hazards of the chemicals they produce or import and to transmit this information to employer-users by means of Material Safety Data Sheets (MSDS') and labels. The employer is required to provide hazard information to their employees by means of labels, MSDS' and training. Employer-users must be in compliance with all provisions of the HCS by May 25, 1986. A comprehensive written "Hazard Communication" program must be developed and implemented by all employers for their employees. The program must include an inventory of all chemicals, assessment of hazard potential, the filing and availability of MSDS', provisions for procurement of chemicals, container labelling, and an employee training program.

The general intent and requirements of the federal statute are similar to those of the various State Right-to-Know Law programs. A manuscript which appeared in the May, 1985 issue of Plating and Surface Finishing entitled "OSHA Hazard Communication and State Right-to-Know Laws" provides further information regarding a comparison of federal and state standards.

At the present time, it appears that the federal law will pre-empt the state Right-to-Know laws affecting manufacturing industry. In a recent ruling, the United States Court of Appeals for the Third Circuit (October 10, 1985, Nos. 85-5087, 85-5088, and 85-5095) and the United States District Court for the Middle District of Pennsylvania (December 12, 1985, No. 85-1027) pre-empted sections of the New Jersey and the Pennsylvania laws applicable to manufacturing industry in the SIC Codes 20-39. Only selected portions were pre-empted by the "Federal Hazard Communication" Standard. Other pre-emption cases are pending a final decision by the courts in the states of Massachusetts, Illinois, New Mexico, and West Virginia.

On November 27, 1985 OSHA issued an Advance Notice of Proposed Rulemaking to expand the scope of the Hazard Communication Standard to include employees in non-manufacturing sectors. This Advance Notice came in response to a recommendation by the National Advisory Committee on Occupational Safety and Health (NACOSH) to OSHA that the scope of the current HCS be expanded to cover all employees in all industries regardless of SIC Code. In addition, OSHA is considering re-opening the rule to clarify several specific issues. A decision to expand the scope of the HCS and re-open the rule will be made following review of public comment by OSHA in 1986.

Until final pre-emption decisions have been made by the courts, manufacturing industry in many states will have to comply with both State Right-to-Know Laws and the Federal Hazard Communication Standard. It is highly likely however, that the courts, quite possibly the Federal Supreme Court, will pre-empt State Right-to-Know Laws for those portions applicable to manufacturing industry. Therefore, the requirements for establishing a written, effective and comprehensive Hazard Communication program to help ensure compliance with the Federal HCS must be a priority for manufacturing industry.

The following activities should be followed when establishing a Hazard Communication program.

1. Chemical Inventory

The chemical inventory is probably the most difficult task to accomplish if the employer routinely uses hundreds of chemicals, which is usually the case in most electroplating/metal finishing facilities. Supervisory personnel play a key role in completion of the chemical inventory. It should be their primary responsibility to compile a list of all chemicals being used in their respective locations. During the inventory, an assessment should be made concerning the use and storage of chemicals. Chemicals no longer used should be properly disposed to eliminate the unnecessary risk of exposure. If not already established, a chemical procurement procedure should be developed. An individual in the Purchasing Department, a designated "Chemical Procurement Officer", should be assigned the responsibility for procurement of any and all chemicals used in the facility and maintaining and updating the inventory, as required, with the assistance of supervisory personnel. Each department should not be allowed to procure chemicals on an individual basis. Centralized procurement from an approved list of chemicals affords management control. The list can also be reviewed by safety and health personnel to help ensure that the least toxic chemicals are being used for the various process operations. Appropriate equipment and facilities can also be defined regarding the chemicals use, transport, and storage.

2. Obtaining Material Safety Data Sheets

Material Safety Data Sheets (MSDS') must be obtained for all chemicals before a determination can be made as to its hazardous nature and inclusion on the OSHA source lists. A standard form letter requesting the provision of MSDS' which meet the HCS requirements should be sent to all manufacturers and distributors at the time of initial purchase. Do not assume that MSDS' obtained in the past from manufacturers and distributors, for chemicals currently used, are the most recent editions. A copy of all written requests for MSDS' should be filed for future reference and attached to the original MSDS once it is received by the employer. Any purchase orders for chemicals procured by the Chemical Procurement Officer should have a blanket statement attached which may read:

> "The Federal Hazard Communication Standard 29 CFR Part 1910.1200 requires manufacturers and distributors to label and make available MSDS' for toxic or hazardous substances. This company's acceptance of your performance under this purchase order is conditioned upon your providing container labels and MSDS' which comply with the law."

Labelling requirements will be discussed further in a separate section.

3. Chemical Evaluation

Once the current MSDS has been obtained, the MSDS must be evaluated to determine whether the chemicals are considered toxic or hazardous as defined by OSHA. To make this determination, the employer must have the following source lists available:

(1) OSHA, 29 CFR Part 1910, General Industry Standards, Subpart Z, Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402, $12.00;

(2) Threshold Limit Values for Chemical Substances and Physical Agents in the Work Environment, (Published Annually), American Conference of Governmental Industrial Hygienists, 6500 Glenway Avenue, Building D-5, Cincinnati, OH 45211, $5.00;

(3) National Toxicology Program, Annual Report on Carcinogens, P.O. Box 12233, Research Triangle Park, North Carolina 27709;

(4) International Agency for Research on Cancer, Monographs, Supplement 4, World Health Organization, Publications Centre, 49 Sheridan Avenue, Albany, NY 12210, $30.00.

The following substances are exempt from the requirements of the HCS:

(1) Any pesticide as defined in the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA);

(2) Any food, food additive, color additive, drug, or cosmetic as defined in the Food, Drug, and Cosmetic Act (FDCA);

(3) Any alcoholic beverage for non-industrial use as defined in the Federal Alcohol Administration Act (FAAA);

(4) Any consumer product as defined in the Consumer Product Safety Act (CPSA) and Federal Hazardous Substances Act (FHSA);

(5) Wood or wood products, tobacco or tobacco products;

(6) Articles and foods, drugs, or cosmetics intended for personal consumption by employees while in the workplace.

If it is questionable whether a substance is considered toxic or hazardous, either contact the nearest OSHA office or assume it is toxic or hazardous and include it in your Hazard Communication Program as a regulated chemical.

A list of the hazardous/toxic chemicals known to be present in the workplace using an identity that is referenced on the appropriate MSDS must be compiled for the workplace as a whole or for individual work areas.

4. The MSDS

The Federal HCS requires MSDS' to contain certain information about the hazardous/toxic components of chemicals. Employers must therefore review MSDS' for completeness. The employer will not be held responsible for inaccurate information provided, but will be responsible for ensuring that MSDS' are complete and acceptable. The employer must ensure that the following information is provided on the MSDS: the chemical identity, Chemical Abstracts Service (CAS) number and common name; physical and chemical characteristics; physical hazards; health hazard; routes of entry; OSHA permissible exposure limit, and ACGIH Threshold Limit Values; whether the hazardous chemical is a listed carcinogen; precautions for safe handling; control measures including engineering/work practice controls and personal protective equipment; emergency and first-aid procedures; date of preparation; name, address, and phone number of manufacturer or distributor; and any other information the manufacturer feels is necessary to provide. Blank spaces are not permitted on MSDS'; spaces should be marked when information is not found or not applicable. If MSDS' are determined to be incomplete or unacceptable, employers have the responsibility to contact the chemical manufacturer, importer or distributor to obtain an MSDS with information required by the HCS. Attempts to obtain additional information from manufacturers, importers or distributors should be documented by letters or logs of telephone requests. If the employer does not receive requested information and has documented his attempts, the OSHA Area Director can assist the employer on a direct request basis.

A revised MSDS has been proposed by OSHA which would replace the existing OSHA Form 20 and is currently under final review by the Office of Management and Budget (OMB). Refer to Enclosure I for a copy of the proposed MSDS. This new MSDS, when properly filled out, will help manufacturers to meet the MSDS requirements of the HCS. The main purpose of the new MSDS is to assist chemical manufacturers and employers that do not want to develop their own MSDS forms. At this time, it is questionable when the form would be ready for public distribution.

Copies of all MSDS' for hazardous chemicals must be maintained in the workplace. MSDS' must be readily accessible during each workshift to employees when they are in their work areas. It is recommended that copies of all MSDS' be kept by the Personnel Department, Safety and Health/Medical Department, and Security Department. Each department or work area supervisor should maintain a file of MSDS' for the chemicals used in that area. Additionally, as a precautionary measure, MSDS' for chemicals not considered hazardous or toxic by OSHA definition should also be maintained.

5. Labels and Other Forms of Warning

An individual should be designated responsible for ensuring the adequate labelling of in-coming and in-plant containers. The individual should ensure that all in-coming chemical containers are labelled by the manufacturer, importer or distributor, with the identity of the hazardous chemicals, appropriate hazard warnings, and name and address of the manufacturer. Containers should not be accepted upon delivery if the required information is not provided. A log should be kept by the responsible individual of all chemicals received, indicating that containers have been inspected for compliance with the labelling requirements of the HCS.

Each container of hazardous chemicals used in the workplace must also be labelled with the identity of the hazardous chemical ingredient(s) and appropriate hazard warnings. The employer is not required by the standard to label portable containers, into which hazardous chemicals are transferred from labelled containers, which are intended only for the immediate use of the employee who performs the transfer. Immediate use means the hazardous chemical will be under the control of and used only by the person who transfers it from a labelled container and only within the work shift in which it is transferred. It is recommended however, that all containers of hazardous chemicals be labelled to reduce potential exposures to other personnel working in the area.

On stationary process containers, such as plating tanks, alternative means such as signs, placards, process sheets, batch tickets, operating procedures, or other written materials may be used instead of affixing labels to the containers. The written alternatives to labelling must identify the containers to which they are applicable and contain the identity of the hazardous chemicals and hazard warnings. The written alternatives must be readily accessible to employees in the work area throughout the workshift. It is advisable to post the placard, batch ticket, etc. as close as possible to the process. A plastic envelope or coating can be used to protect the written material from water-chemical damage.

To ensure that all containers are labelled appropriately, a labelling program listing all hazardous chemicals and the applicable hazard warnings required on the container should be kept. A description of the written alternatives, i.e. signs, placards, process sheets, etc. should be included in the labelling program. A procedure must also be established for review and update of label information. An inspection of areas in the facility where hazardous chemicals are used should be conducted on a routine basis and a record kept to help ensure that appropriate labels are in place at all times on all containers requiring labels. Although it is not required, pipes transporting hazardous materials should be labelled, color-coded or numbered for ease of identification should a rupture or leak occur. The American National Standards Institute (ANSI) has developed a consensus standard entitled, "Scheme for the Identification of Piping Systems", 1981, that can be used as a guideline to pipe labelling. Copies of this standard can be obtained from ANSI, 1430 Broadway, New York, New York, 10018.

6. Training

A Hazard Communication training program must be established and administered to employees potentially exposed to hazardous chemicals at the time of their initial assignment and whenever a new hazard is introduced into their work area. The employee training program must include:

(1) Information on the requirements of the HCS;

(2) A description of any processes or operation in their work area where hazardous chemicals are used;

(3) The methods utilized to detect the presence or release of a hazardous substance in the work area;

(4) The physical and health hazards of the chemicals used in the work area;

(5) Hazards associated with non-routine tasks;

(6) The hazards of chemicals in unlabelled pipes;

(7) The availability and use of personal protective equipment;

(8) Work practices;

(9) Emergency procedures;

(10) An explanation of the labelling system and the MSDS; and

(11) How employees can obtain and use the hazard information available to them.

An excellent approach to meet the training requirements outlined above is to first develop a generic training manual for employee distribution prior to conducting formal training sessions. The training manual should contain general information that all employees potentially exposed to hazardous chemicals in the workplace are required to know. The manual should also contain a section on basic chemical safety that outlines general precautions to be taken with all chemicals, as well as for specific categories of chemicals (i.e., acids, alkalis, organic solvents, cyanides, flammables metals, oxidizers, reactives and other unique chemicals), personal protective equipment, and respiratory protection. A list of safety and health reference publications should also be provided as a source of further information employees may wish to obtain. In addition to a generic training manual, other training manuals, booklets and/or pamphlets should be developed and used to help train employees handling hazardous chemicals and conducting hazardous processes and non-routine tasks unique to their particular job assignment.

Written training should be supplemented with verbal training sessions to enforce the importance of a Hazard Communication program and allow for questions and answers. Several excellent audio-visuals are available regarding Hazard Communication and chemical handling and use, to supplement written and verbal training. Carefully screen and only utilize material prepared by experienced professional organizations such as the National Safety Council, Bureau of National Affairs, and American Society of Safety Engineers.

Several different approaches can be utilized to conduct training sessions. One approach is to assign a qualified individual (e.g., nurse, industrial hygienist, safety professional, or chemist) to conduct both generic and specific training to all employees affected by the Hazard Communication program. Another and usually a more successful approach, is for the qualified individual to train only department supervisors who in turn will be responsible for training department personnel, with assistance from the qualified individual, as necessary. This is a more favored approach because it focuses on and assigns direct responsibility to the Department Supervisor who is actively involved in the day to day supervision of personnel who routinely handle and use chemicals in their respective work areas.

Regardless of the approach utilized to train personnel however, it is the responsibility of the Department Supervisor to ensure that the established procedures for the proper use and handling of chemicals are followed. The supervisor should routinely observe the methods being used and conduct review sessions on Hazard Communication to help ensure all personnel in the work area fully understand their responsibilities when handling and using hazardous chemicals. The supervisor should also maintain the MSDS' for the work area and have them readily available during each work shift for employees at their work areas. Supervisor involvement is critical to help ensure the long-term success of the Hazard Communication program by making it a routine part of his/her daily activities and interface with employees.

It is not required by the HCS, but recommended that employees complete an employee training documentation sheet and that it be kept in their personnel file as a permanent record of training. These records could be helpful to OSHA Compliance Safety and Health Officers (CSHO's) to assess a company's compliance with the standard should an inspection be conducted. As part of the OSHA inspection procedures for the Hazard Communication Standard, CSHO's will be required to interview a select, representative number of employees to assess the adequacy of the training program. These interviews will provide general information to the CSHO. If the CSHO detects that training is not conducted or is conducted in a fashion that does not meet the intent of the standard, a closer review of the written program and its implementation may be necessary. The establishment and implementation of a thorough training program that meets the requirements of the HCS is extremely important and necessary to help reduce potential chemical injury and illness and ensure regulatory compliance.

7. Trade Secrets

Under the HCS final rule published on November 25, 1983, the chemical name and other specific identification of a hazardous chemical can be withheld from an MSDS by the manufacturer. Under the original ruling, the chemical name was required to be made available to only health professionals (i.e., physicians, toxicologists, industrial hygienists, and epidemiologists) for emergency or first-aid treatment, regardless of the existence of a written statement of need or a confidentiality agreement, and in non-emergency situations upon written request from a health professional.

On November 27, 1985, however, OSHA issued an Interim Final Rule amending the HCS to extend access to trade secret chemical identity in both emergency and non-emergency situations to employees and their designated representatives who demonstrate a "need-to-know" the information and the means to maintain its confidentiality. A final determination on the Interim Final Rule will be made after OSHA receives and reviews public comment. At the same time, a proposal was issued to recommend the inclusion of occupational health nurses as "health professionals" entitled to chemical information when treating an exposed worker in a non-emergency situation.

It is recommended that a copy of all trade secret MSDS', if any, be kept in a separate file at all locations in the facility where MSDS' are made available, along with a list of manufacturer's and their telephone numbers, should an emergency situation arise requiring immediate chemical identity for first-aid action. Should a health professional or other designated employee be denied access to trade secret information, the matter may be referred to OSHA for enforcement proceedings.

8. Written Hazard Communication Program

Once all of the Hazard Communication program requirements have been defined, (e.g., labelling procedures, maintaining acceptable MSDS, training, and listing of hazardous chemicals, etc.), a written document to formalize the company's Hazard Communication program can be easily prepared and made available to employees, their designated representatives, and the Assistant Secretary of Labor and the OSHA Area Director upon request.

A key factor that must be carefully considered when developing the written HCS is personnel responsibilities. In order to implement and maintain an effective Hazard Communication program, appropriate personnel must be selected to administer the program and help ensure continued compliance. The ultimate success of the program requires active participation by upper management, purchasing agents, receiving personnel, supervisory personnel, and health professionals. Responsible individuals should be selected and their responsibilities defined and incorporated into the written Hazard Communication program.

Lastly, in addition to the requirements previously discussed, the employer must develop a plan outlining the methods he will use to inform outside contractors working in the employer's workplace, of the hazardous chemicals to which the contracted employees may be exposed while performing work on-site and any suggestions or requirements for appropriate protective measures. A suggested method of informing outside contractors of potential exposures is to conduct a brief informative training session prior to initiating work, highlighting the hazards associated with the chemicals, distributing and reviewing MSDS' for the chemicals of concern and outlining in writing, areas of the facility where access by the contractor will be restricted. It is recommended that the contractor and his employees sign a documentation sheet stating that they have been informed of the hazards associated with chemicals they may be exposed to while performing their work and where required or suggested, to take appropriate protective measures. The protective measures required or suggested should be listed for each individual on the documentation sheet.

Conclusion

The HCS is essentially a performance standard. Although it allows employers the flexibility to develop a Hazard Communication program that fits the needs of their particular facility, it is specific in stating the goals that must be achieved. Once the goals are achieved and all aspects of the program are in place and functional, industry should hopefully see increased employee job dedication and a reduction in the incidence of routine and non-routine chemical source injury and illness as a result of increased employee awareness of chemical hazards in the workplace.

The following Summary of implementation activities can be used as a guideline to develop and implement a hazard communication program.

- Inventory all chemicals used throughout the facility.
- Identify individuals responsible for procuring, evaluating, and maintaining MSDS'.
- Establish a procedure which requires the routine procurement of MSDS' through Purchasing Department channels.
- Identify listed substances. Initially assume that all process and janitorial/maintenance substances are listed.
- Collect and evaluate MSDS'. Send form letters to chemical manufacturers and distributors requesting additional data, etc., as necessary. Keep a record of all such correspondence.
- Maintain and make readily accessible to employees during each workshift, copies of all MSDS'.

- Develop and implement an employee training program. Training suggestion: Categorize listed substances by nature of hazard and discuss by category. Use commercially available training aids.

- Train all employees before May 27, 1986 or earlier. Train employees at the time of initial assignment, and whenever a new hazard is introduced into the work area.

- Maintain a record of training. Complete attendance sheets.

- Establish procedures for handling trade secret information.

- Ensure adequate labelling of containers. Consult state requirements.

- Develop a plan to be used to inform outside contractors of hazards associated with chemicals they may be exposed to while working in your facility.

- Maintain a copy of the OSHA Hazard Communication Standard.

- Establish a community access policy, if required by state law.

- Formalize all policies and procedures into a written Hazard Communication Program.

OSHA DRAFT VOLUNTARY FORM FOR MATERIAL SAFETY DATA SHEETS

DRAFT

Material Safety Data Sheet
May be used to comply with
OSHA's Hazard Communication Standard,
29 CFR 1910.1200. Standard must be
consulted for specific requirements.

U.S. Department of Labor
Occupational Safety and Health Administration
(Non-Mandatory Form)

IDENTITY *(As Used on Label and List)*	*Note: Blank spaces are not permitted. If any item is not applicable, or no information is available, the space must be marked to indicate that.*

Section I

Manufacturer's Name	Emergency Telephone Number
Address *(Number, Street, City, State, and ZIP Code)*	Telephone Number for Information
	Date Prepared
	Signature of Preparer *(optional)*

Section II — Hazardous Ingredients/Identity Information

Hazardous Components (Specific Chemical Identity; Common Name(s))	OSHA PEL	ACGIH TLV	Other Limits Recommended	% *(optional)*

Section III — Physical/Chemical Characteristics

Boiling Point		Specific Gravity (H_2O = 1)	
Vapor Pressure (mm Hg.)		Melting Point	
Vapor Density (AIR = 1)		Evaporation Rate (Butyl Acetate = 1)	

Solubility in Water

Appearance and Odor

Section IV — Fire and Explosion Hazard Data

Flash Point (Method Used)	Flammable Limits	LEL	UEL

Extinguishing Media

Special Fire Fighting Procedures

Unusual Fire and Explosion Hazards

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ENCLOSURE I

DRAFT

Section V — Reactivity Data

Stability	Unstable		Conditions to Avoid
	Stable		

Incompatability *(Materials to Avoid)*

Hazardous Decomposition or Byproducts

Hazardous Polymerization	May Occur		Conditions to Avoid
	Will Not Occur		

Section VI — Health Hazard Data

Route(s) of Entry: Inhalation? Skin? Ingestion?

Health Hazards *(Acute and Chronic)*

Carcinogenicity: NTP? IARC Monographs? OSHA Regulated?

Signs and Symptoms of Exposure

Medical Conditions
Generally Aggravated by Exposure

Emergency and First Aid Procedures

Section VII — Precautions for Safe Handling and Use

Steps to Be Taken in Case Material Is Released or Spilled

Waste Disposal Method

Precautions to Be Taken in Handling and Storing

Other Precautions

Section VIII — Control Measures

Respiratory Protection *(Specify Type)*

Ventilation	Local Exhaust	Special
	Mechanical *(General)*	Other

Protective Gloves	Eye Protection

Other Protective Clothing or Equipment

Work/Hygienic Practices

S12

AIR POLLUTION CONTROL EQUIPMENT FOR SELECTED PLATING SHOP PROCESSES BASED ON EMISSION TEST RESULTS

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I. INTRODUCTION

The purpose of the plating shop emissions test program discussed in this paper is twofold:

A. Determine which processes require air pollution control equipment.

B. Determine the most cost effective control technology for processes requiring air pollution control equipment.

The Navy operates plating shops at shipyards and aircraft refurbishing facilities nationwide. Common practice in the past 10 to 15 years has been to install pollution control equipment, usually wet scrubbers, on any shop process requiring exhaust ventilation. This is a very conservative approach, resulting primarily from a lack of reliable emissions data on plating shop processes.

Wet scrubbers* typically add two to three inches water gauge (WG) static pressure to the exhaust fan load. Added static pressure load costs several thousand dollars a year in exhaust fan electrical demand. Scrubber water supply systems and water recirculation systems require regular maintenance, and scrubber wastewater usually requires treatment prior to disposal. The operation of wet scrubbers on processes that produce very low emissions is unnecessary, and results in additional plant energy costs and equipment maintenance costs.

Wet scrubbers are designed to absorb water soluble gases and to remove mist larger than 8 microns (um) diameter. A mist eliminator is included within the wet scrubber to remove mist generated in the scrubber's turbulent gas absorption zone. Wet scrubbers are unnecessarily complex for processes generating only mist emissions in the 8 um range, such as the chromium plating process. Fine mists less than 3 um diameter are not removed effectively by this scrubber design. Processes that primarily generate fine mist require specialized air pollution control equipment.

The following categories of processes were tested during the emissions testing program:

A. Hard Chromium Plating (Cr).

B. Acid Stripping (HCl, H_2SO_4).

C. Caustic Cleaning (NaOH).

*Wet scrubber: Thin-bed packed tower, vertical counterflow type.

T1

D. Heavy Metal Plating (Cd, Cu, Ag).

E. Chromic Acid Bright Dip (Cr).

II. TEST METHODOLOGY

The sampling train design was based on the following assumptions:

A. Pollutants being sampled will be present both as mist (liquid phase), and as gas (gas phase).

B. All pollutants being sampled are readily water soluble.

C. A modified EPA Method 5 (particulate concentration) sampling train was used initially. This sampling system was effective in determining total emissions regardless of phase. However, we realized that the addition of a high efficiency cyclone, followed by a filter capable of removing virtually all remaining mist, would allow us to obtain a two-stage particle size distribution and liquid phase/gas phase percentages. The two-stage particle size distribution obtained from the mass emissions sampling train was used as a confirmation of cascade impactor results obtained during testing of hard chromium plating emissions.

Exhaust lines containing an air pollution control device were sampled simultaneously at the control device inlet and outlet to determine collection efficiency. The duration of sampling runs was generally 90 minutes. Collected samples were analyzed using wet chemistry (chloride, sulfate, cyanide) or atomic absorption spectrophotometry (metals).

A cascade impactor was initially used on all processes to characterize the particle size distribution of the liquid phase of the pollutant emission. Several processes had such low emissions that insufficient quantities of mist were generated to produce usable particle size data. Only the hard chromium plating process generated sufficient quantities of liquid phase emissions to obtain consistent impactor results.

Determining the particle size distribution of hydrochloric acid (HCl) mist generated during metal stripping operations presented a special problem. Attempts made with the cascade impactor produced erratic results, and a new approach was sought. We successfully employed a "sedimentation chamber"+ to size the HCl mist. A gas sample was drawn into an impinger modified to contain a silver-coated cover slide connected to the impinger stem. This sedimentation chamber was sealed for 24 to 48 hours following exposure to exhaust gas, to allow the HCl mist to settle onto the cover slide. The cover slide was then placed in a scanning electron microscope (SEM) and photographed under high magnification. Particles were sized and counted from the SEM photograph.

+Patent pending.

Tank loads were maintained at maximum operating levels during the emission tests. High power levels were maintained in the electroplating tanks and in the electrocleaning tanks. Tank loading data and power level data are presented with the results for each process tested.

III. RESULTS

The results of the emission testing program are grouped into the following five process categories:

A. Hard Chromium Plating (Cr).

B. Acid Stripping (HCl, H_2SO_4).

C. Caustic Cleaning (NaOH).

D. Heavy Metal Plating (Cd, Cu, Ag).

E. Chromic Acid Bright Dip (Cr).

Both the hard chromium plating process and the acid stripping process generate sufficient emissions at maximum tank loading to justify a control device. A mesh-pad mist eliminator proved to be very effective on chromic acid mist, and was the least costly control device tested on the hard chromium process. HCl emissions are primarily gas phase, and are effectively controlled by a wet scrubber. A significant percentage (16%) of HCl emissions are in the form of mist less than 2 um diameter, and a wet scrubber has limited effectiveness on HCl mist in this size range. Nuisance plumes of HCl mist were visible during periods of high tank loading. High efficiency fiberbed mist eliminators can be added in series with a wet scrubber to remove the HCl mist, though the fiberbed mist eliminator adds considerable static pressure to the exhaust fan load.

Caustic cleaning, heavy metal plating, and chromic acid bright dip produce low emissions, well below any applicable emission standard. Emissions from these processes are insufficient to warrant the use of pollution control equipment.

The regulatory procedures used to set source emission standards for the pollutants studied during this test program vary. Test 1 and test 3 were performed at a naval shipyard in Southern California. The California South Coast Air Quality Management District (SCAQMD) requires "best available control technology" (BACT) on new industrial sources such as plating shops. The definition of BACT for specific processes is left to the discretion of the SCAQMD engineer reviewing the process.

Test 2 was performed at a naval shipyard located in coastal Virginia, in Region VI of the Virginia Air Pollution Control Board (VAPCB). The VAPCB sets limits for specific pollutants during the permit application process for new industrial sources. Emission limits for specific processes are set based on data available at the time of the construction permit application. Compliance with emission limits for selected processes must be demonstrated following construction of the facility.

Indoor air quality standards were used in this study to determine which processes required pollution control equipment. Control equipment was considered necessary for processes generating emissions in concentrations exceeding the Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL). "PEL" is defined as the maximum allowable 8-hour, time-weighted-average airborne concentration (mg/m^3) of a chemical in the workplace.

Rarely, in peacetime, do naval shipyard plating shops approach production capacities. To reach the tank loading expected during full production, "dummy" loads were added to tanks undergoing testing. Tank loading information is presented for each process tested.

The tank solution conditions for each process are listed in Table 1.

A. Hard Chromium Plating.

1. General.

Hard chromium plating at naval shipyards is employed primarily to build up worn bearing surfaces on motor and generator shafts used aboard ships. The peacetime production rate is sporadic, and steel plate "dummies" were added during emission testing to simulate full production conditions.

The rate of deposition is directly related to the current density used in the plating tank, and a current density of approximately 100 amps/ft^2 workpiece area is typically used in Navy chromium plating operations.

The current efficiency of the chromium electroplating process is low, typically 10-20%. Current efficiency is defined as the actual quantity of current used for metal deposition divided by the total current input to the plating bath. The hydrolysis of water proceeds more readily than the depositon of chromium, and 80-90% of the current input is consumed by the hydrolysis reaction. Hydrogen is evolved at the cathode and oxygen evolved at the anode. Chromic acid mist is generated as the gas bubbles break through the surface of the bath.

Chromium is added to the plating bath in the form of chromic anhydride, CrO_3, a reddish-brown powder commonly called "chromic acid." The valence state of chromium in CrO_3 is hexavalent, Cr^{+6}. It follows that Cr^{+6} is the predominant ionic state of chromium in the plating bath. A minute amount of trivalent chromium, Cr^{+3}, is also present in the plating bath as an impurity. Cr^{+3} is kept below 1% of the total chromium in solution to minimize the deleterious effects Cr^{+3} has on the bath operating characteristics.

Collected emission samples were analyzed for total

TABLE 1. TANK SOLUTION CONDITIONS

PROCESS	SOLUTION CONCENTRATIONS	TEMPERATURE °F
Hard chromium plating	CrO_3 = 200 - 250 g/l	130°F
Decorative chromium plating	CrO_3 = 250 g/l	115°F
Hydrochloric acid strip	HCl = 25 - 29% by volume	Room
Sulfuric acid strip	H_2SO_4 = 50% by volume	Room
Caustic etch -aluminum	NaOH = 75 g/l	150°F
Electrocaustic	NaOH = 280 g/l	165°F
Cadmium plating	Cd^{++} = 26 g/l CN^- = 62 g/l	Room
Copper plating	Cu^{++} = 49 g/l CN^- = 53 g/l	140°F
Silver plating	Ag^+ = 40 g/l CN^- = 53 g/l	Room
Aluminum dip	CrO_3 = 20 g/l	Room
Brass bright dip	CrO_3 = 30 g/l	Room
Brass seal	CrO_3 = 20 g/l	Room
Aluminum conversion coat	CrO_3 = 16 g/l	Room

g/l = grams/liter

chromium, with the assumption that the total chromium concentration is essentially equivalent to the Cr^{+6} concentration. Cr^{+6} is reduced to Cr^{+3} in aqueous solutions containing reducing agents, and three to five days elapsed between the emission tests and laboratory analysis of the sample solutions. A portion of the Cr^{+6} was reduced to Cr^{+3} in many of the sample solutions prior to laboratory analysis.

2. Emission Test Results.

Uncontrolled Cr^{+6} emission rates were similar during test 1 and test 2, with an average emission concentration of 0.56 mg/m^3, well above the OSHA PEL of 0.1 mg/m^3. The wet scrubber averaged 92% removal efficiency during test 1. The mesh-pad mist eliminator averaged 95% removal efficiency during test 2. Both the wet scrubber and the mist eliminator reduced the Cr^{+6} emission rate below the OSHA PEL of 0.1 mg/m^3. Mass emissions test results are shown in tables 2 and 3.

Cr^{+6} is emitted exclusively as chromic acid mist. Particle size distribution tests show an average chromic acid mist mass mean diameter (MMD) of 8 um. The MMD was consistent at both test sites. Results of the particle size distribution tests are shown in tables 4 and 5.

3. Pollution Control Equipment.

The relatively large particle size of chromic acid mist explains the high collection efficiency of the control devices tested. The mesh-pad mist eliminator is superior to the wet scrubber in this application, though both control devices performed well. The mist eliminator produces a concentrated, low volume chromic acid effluent, potentially available for re-use. Also, the mist eliminator is a simpler device, lacking the continuous water recirculation system used in a wet scrubber.

B. Acid Stripping.

1. General.

Acid stripping is used in Navy plating shops to remove rust and protective metal coatings from steel. The ventilation system tested during tests 1 and 3 consists of two HCl tanks and one sulfuric acid electrostrip tank exhausted through a wet scrubber. The emissions generated during these tests realistically reflect the effect of maximum workpiece loading in the tanks. Results from test 1 are suspect due to flooding in the lower portion of the exhaust duct during testing, and test 1 results are not used in this paper.

A 55-gallon drum of concentrated HCl was lowered into an empty tank connected to a wet scrubber during test 2. This plating shop was not using the HCl strip tank at the time of the test. The HCl drum was placed in the empty tank to allow HCl removal efficiency testing on the wet scrubber. Alumimum was "sacrificed" in the HCl to generate

HARD CHROMIUM PLATING
TABLE 2. PROCESS DATA--MASS EMISSIONS TESTING

	NUMBER OF TANKS PER EXHAUST SYSTEM	TOTAL TANK CAPACITY PER EXHAUST SYSTEM (GAL)	AVE. WORKPIECE AREA PER TANK (FT^2)	AVE. VOLTAGE PER TANK (V)	AVE. AMPS PER TANK (A)
TEST 1	4	8750	14.5	7.8	1425
TEST 2	1	1900	31.0	6.6	2480

HARD CHROMIUM PLATING
TABLE 3. RESULTS--MASS EMISSIONS TESTING

	CONTROL DEVICE	NUMBER 90-MINUTE SAMPLING RUNS	AVERAGE EXHAUST FLOWRATE (SCFM)	SPECIE	OSHA PEL*	UNCONTROLLED (INLET) CONCENTRATION		CONTROLLED (OUTLET) CONCENTRATION		AVERAGE COLLECTION EFFICIENCY (%)
					(mg/m^3)	(mg/m^3)	(lb/hr)	(mg/m^3)	(lb/hr)	
TEST 1	Wet Scrubber	4	29500	Cr^{+6}	0.1	0.51	.056	0.04	.005	92
TEST 2	Mesh Pad Mist Eliminator	3	8900	Cr^{+6}	0.1	0.61	.019	0.03	.001	95

*PEL = Permissible Exposure Limit. The PEL is the maximum time weighted average concentration allowable over an 8-hour period. This is an indoor air quality standard.

T9

HARD CHROMIUM PLATING
TABLE 4. PROCESS DATA--PARTICLE SIZE TESTING

	NUMBER OF TANKS PER EXHAUST SYSTEM	TOTAL TANK CAPACITY PER EXHAUST SYSTEM (GAL)	AVE. WORKPIECE AREA PER TANK (FT^2)	AVE. VOLTAGE PER TANK (V)	AVE. AMPS PER TANK (A)
TEST 1	4	8750	14.9	8.2	1610
TEST 2	1	1900	18.5	7.0	1650

HARD CHROMIUM PLATING
TABLE 5. RESULTS--INLET PARTICLE SIZE DISTRIBUTION TESTING

	NUMBER OF 4-HOUR SAMPLING RUNS	AVERAGE MASS MEAN PARTICLE DIAMETER (um)
TEST 1	2	7.6
TEST 2	2	8.0

Specific gravity of chromic acid mist = 1.15

emissions, as the shop had few workpieces available.

Immersing aluminum in concentrated HCl causes an extremely violent reaction, generating a visible cloud of HCl mist. This reaction is more volatile than reactions observed during typical acid stripping operations, and uncontrolled HCl emissions generated during test 2 were much greater than those observed during test 3. Only the percentages of liquid and gas phase HCl emissions are used from test 2 results, due to the atypical nature of the reaction.

The OSHA PEL is used as the standard to compare test results. The OSHA PEL is 7.0 mg/m^3 for HCl.

The modified EPA Method 5 sampling train used during emission testing allowed measurement of percentages of HCl in both the gas phase and the liquid phase. The relative quantities of gas phase and liquid phase HCl are important in determining the type of air pollution control device necessary. Gas phase HCl is very soluble in water and is readily removed by a wet scrubber. Liquid phase HCl is a fine mist with a mass mean diameter of less than 2 um, and removal by a wet scrubber is limited.

A cascade impactor was initially used to determine the size distribution of the HCl mist. A four-hour sampling run did not show any visual evidence of HCl mist collection on the impactor stages, so an alternative method was used to obtain usable particle size distribution data. A sedimentation chamber was used to optically size the HCl mist.

2. Emission Test Results

Tables 6, 7, and 8 contain results of the HCl emission tests. The average uncontrolled HCl emission rate was 20.6 mg/m^3, approximately three times the OSHA PEL of 7.0 mg/m^3. Approximately 84% of emissions were in the gas phase, with the remaining 16% in the form of mist. A mass mean particle diameter of 1 to 2 um was determined for the HCl mist. The uncontrolled H_2SO_4 emission rate was at the lower detectable limit for the analytical method used.

The wet scrubber averaged 99% removal efficiency on gas phase HCl, and 76% removal efficiency on HCl mist. The overall HCl removal efficiency was 95%.

3. Pollution Control Equipment

The wet scrubber averaged 95% removal efficiency on HCl generated in the acid stripping tanks, adequate removal efficiency for this application. Despite relatively high HCl removal efficiency, a green plume was visible at the stack outlet under high tank loading conditions. The visible plume is attributed to HCl mist passing through the scrubber.

More efficient removal of the HCl mist component can be

ACID STRIPPING
TABLE 6. PROCESS DATA--MASS EMISSIONS TESTING

	NUMBER OF TANKS PER EXHAUST SYSTEM	TANK CONTENTS	TANK(S) CAPCITY (GAL)	AVE. WORKPIECE AREA PER TANK (FT^2)	AVE. VOLTAGE (V)	AVE. CURRENT (A)
TEST 1	3	HC1	1300	18	N/A	N/A
		HC1	1300	18	N/A	N/A
		$H_2 SO_4$	1300	9	5.2	860

T13

ACID STRIPPING

TABLE 7. RESULTS--MASS EMISSIONS TESTING

	NUMBER OF 90-MINUTE SAMPLING RUNS	AVERAGE EXHAUST FLOWRATE (SCFM)	OSHA PEL (mg/m^3)	SPECIE	UNCONTROLLED (INLET) CONCENTRATION		CONTROLLED (OUTLET) CONCENTRATION		AVERAGE COLLECTION EFFICIENCY (%)
					(mg/m^3)	(lb/hr)	(mg/m^3)	(lb/hr)	
TEST 3	3	20,900	7.0	HCl	20.6	1.68	0.7	.06	96
			1.0	H_2SO_4	1.4	0.11	0.45	.04	68

ACID STRIPPING
TABLE 8. PERCENTAGE OF UNCONTROLLED HCl EMISSIONS IN LIQUID PHASE AND GAS PHASE

	LIQUID PHASE (%)	GAS PHASE (%)	TOTAL (%)
TEST 2	12	88	100
TEST 3	20	80	100
AVE.	16	84	100

T14

achieved using a fiberbed mist eliminator (FME). A well designed FME can attain 99% removal efficiency on submicron droplets. A wet scrubber in series with a FME will remove virtually all HCl emissions. A disadvantage of the FME is the substantial pressure drop it requires for operation. A pressure drop of 7 in. WG is required across the FME for 95% removal of HCl mist. This compares with a pressure drop of approximately 3 in. WG across the wet scrubber alone. The slight gain in overall HCl removal efficiency, made possible by adding a FME in series with the existing wet scrubber, is countered by the large increase in exhaust fan static pressure. We opted not to add the FME to the wet scrubber because of the large energy demand the FME would place on the exhaust fan.

Two other devices have the potential to work well with a combined liquid/gas phase HCl emission source, the ionizing wet scrubber and the rotary atomizing scrubber. Both devices combine high efficiency gas absorption with submicron particle removal. Though neither device is in use by the Navy, both devices deserve consideration for this application.

C. Caustic Cleaning.

1. General

Sodium hydroxide (caustic) solutions are used extensively in Navy plating shops and chemical cleaning shops. Non-electrical caustic solutions are used to remove oxide layers from aluminum. This is a dip process where parts are immersed for only a few seconds. Electro-caustic solutions are used to remove soil and grease from steel parts. This is a soak process and parts are immersed for periods of a few minutes to several hours. Emissions from an exhaust ventilation line connected to three caustic cleaning tanks were measured during test 1.

2. Emission Test Results

The uncontrolled NaOH emission rate of 0.26 mg/m^3 is substantially below the OSHA PEL standard of 20 mg/m^3. Emission test results are shown in tables 9 and 10. Scrubber efficiency is low, primarily due to the low inlet concentration of NaOH. Air pollution control equipment is unnecessary on caustic cleaning processes.

D. Heavy Metal Plating.

1. General

The term heavy metal plating as used in this project includes the following metals: copper, silver, and cadmium. These metals are plated from cyanide (CN^-) solutions. Copper serves as base metal coating for chromium plating. Silver is plated on bearing surfaces because of its excellent wear resistance. Cadmium is plated onto ship components exposed to salt water, especially fasteners. Cadmium coatings are superior to galvanized (zinc) coatings for marine applications.

CAUSTIC CLEANING
TABLE 9. PROCESS DATA--MASS EMISSIONS TESTING

	NUMBER OF OPERATIONAL CAUSTIC TANKS ON EXHAUST SYSTEM	TANK CONTENTS	TANK CAPACITY (GAL)	AVE. WORKPIECE AREA PER TANK (FT^2)	AVE. VOLTAGE PER TANK (V)	AVE. AMPS PER TANK (A)
TEST 1	2	CAUSTIC - ALUMINUM ETCH	700	22.5	N/A	N/A
		ELECTRO-CAUSTIC	5400	38	7.0	1950

NOTE: Tank loads were lifted every 15 minutes during emission testing.

T17

CAUSTIC CLEANING
TABLE 10. RESULTS--MASS EMISSIONS TESTING

	CONTROL DEVICE	NUMBER OF 90-MINUTE SAMPLING RUNS	AVERAGE EXHAUST FLOWRATE (SCFM)	OSHA PEL	UNCONTROLLED (INLET) CONCENTRATION		CONTROLLED (OUTLET) CONCENTRATION		SCRUBBER COLLECTION EFFICIENCY (%)
				(mg/m^3)	(mg/m^3)	(lb/hr)	(mg/m^3)	(lb/hr)	
TEST 1	Wet Scrubber	4	34,600	2.0	0.26	.034	0.16	.021	38

The current efficiencies of the heavy metal plating processes tested range from 90-100%. Little or no hydrolysis occurs, as the input current is used almost exclusively for metal deposition, and gassing is minimal.

2. Emission Test Results

The uncontrolled cyanide emission rate is well below the OSHA PEL of 5.0 mg/m^3. Emission test results are shown in tables 11 and 12. Emissions averaged 0.04 mg/m^3 and 0.25 mg/m^3, respectively, during test 1 and test 2. A partial explanation for the difference in measured concentrations is the large difference in exhaust airflows maintained in the two exhaust systems, 49500 SCFM versus 7700 SCFM. The tank surface area and the workpiece area were approximately the same during both tests. Air pollution control equipment is not necessary to control cyanide emissions from heavy metal plating baths.

Trace levels of cadmium and copper were measured at both test sites. Cadmium and copper emission rates are well below the applicable OSHA PEL. Silver emissions were below detectable limits.

E. Chromic Acid Bright-Dip.

1. General

Non-electrical chromic acid solutions are used to perform the following functions on aluminum and brass: Removal of oxide layers, surface activation, and conversion coating. Air agitation was employed in several of the tanks undergoing testing.

2. Emission Test Results

The uncontrolled chromic acid emission rate averaged less than .02 mg/m^3, well below the OSHA PEL of 0.1 mg/m^3. Emission test results are shown in tables 13 and 14. Approximately the same concentrations of chromic acid were measured at the scrubber inlet and outlet. An air pollution control device is not necessary on non-electrical chromic acid solutions.

IV. CONCLUSION

Air pollution control equipment is necessary for chromium electroplating processes and for HCl stripping operations. Chromium electroplating emissions are in the form of mist averaging 8 um in diameter, and are removed effectively by a mesh-pad mist eliminator. HCl emissions are primarily gas phase (84%), with the remaining portion (16%) in the form of fine mist less than 2 um in diameter. A vertical, countercurrent wet scrubber can achieve 95% removal efficiency on these mixed phase HCl emissions.

Emissions generated by the caustic cleaning, heavy metal plating, and chromic acid bright-dip processes are well below the conservative OSHA PEL standards used to evaluate emission rates. No emission controls are necessary on these processes.

HEAVY METAL PLATING
TABLE 11. PROCESS DATA--MASS EMISSIONS TESTING

	NUMBER OF TANKS PER EXHAUST SYSTEM	TANK CONTENTS	TANK CAPACITY PER EXHAUST SYSTEM (GAL)	AVE. WORKPIECE AREA PER TANK (FT^2)	AVE. VOLTAGE PER TANK (V)	AVE. AMPS PER TANK (A)
TEST 1	5	Cd^{++}, CN^-	1300	8	4	450
		Cd^{++}, CN^-	1300	7	4	450
		Ni^{++}, Cl^-	1300	4	6	340
		Cu^{++}, CN^-	1300	2	1.1	20
		Ag^+, CN^-	1300	4	2.4	310
TEST 2	4	CN^- STRIP	300	3.5	9.7	210
		Cu^{++}, CN^-	800	12	9.6	570
		Zn^{++}, CN^-	300	4.5	8.5	60
		Cd^{++}, CN^-	500	7.0	9.4	280

HEAVY METAL PLATING
TABLE 12. RESULTS--MASS EMISSIONS TESTING

	CONTROL DEVICE	NUMBER OF 90-MINUTE SAMPLING RUNS	AVERAGE EXHAUST FLOWRATE (SCFM)	SPECIE	OSHA PEL (mg/m^3)	UNCONTROLLED (INLET) CONCENTRATION	
						(mg/m^3)	(lb/hr)
TEST 1	Wet Scrubber	3	49500	CN^-	5.0	.04	.008
				Cd^{++}	0.1	.001	--
				Cu^{++}	0.1	.01	--
TEST 2	None	3	7700	CN^-	5.0	.25	.007
				Cd^{++}	0.1	.001	--

BRIGHT DIP
TABLE 13. PROCESS DATA--MASS EMISSIONS TESTING

	NUMBER OF TANKS PER EXHAUST SYSTEM	TANK CONTENTS	TANK CAPACITIES (GAL)	AVE. WORKPIECE AREA PER TANK (FT^2)
TEST 1	8	Cr^{+6}	1300	3
		Na^+, PO_4	1300	8
		Cr^{+6}	700	9
		Cr^{+6}	700	4.5
		Cr^{+6}	900	6
		Cr^{+6}	900	3
		Cr^{+6}	700	18
		Cr^{+6}	700	24

T22

BRIGHT DIP
TABLE 14. RESULTS--MASS EMISSIONS TESTING

	CONTROL DEVICE	NUMBER OF 90-MINUTE SAMPLING RUNS	AVERAGE EXHAUST FLOWRATE (SCFM)	SPECIE	OSHA PEL (mg/m^3)	UNCONTROLLED (INLET) POLLUTANT CONCENTRATIONS		CONTROLLED (OUTLET) POLLUTANT CONCENTRATION	
						(mg/m^3)	(lb/hr)	(mg/m^3)	(lb/hr)
TEST 1	Wet Scrubber	3	44100	Cr^{+6}	0.1	.02	.004	.02	.004

T23

BIBLIOGRAPHY

1. Federal Register, Environmental Protection Agency, Standards of Performance for New Stationary Sources, Vol 40, Part 60, August 1977.

2. American Society of Mechanical Engineers, Performance Test Code (PTC) 28 Determining Properties of Fine Particulate Matter, (draft edition).

3. Pollution Control Systems Corporation, Operations Manual, Pilat Mark 3 and Mark 5 Source Test Cascade Impactors, Seattle, Washington, January 1983.

4. G. Lowrie Fairs, Sampling of Dust Laden Gases, Trans-Industrial Chemical Engr. Journal (Brit.), Vol 29, p 15, 1951.

5. Harrington Industrial Plastics, Inc., Anaheim, California, Air Pollution Control Equipment Specifications. Phone No. (714) 879-9030.

6. Heil Process Equipment Company Bulletin B-730-2, Heil Fume Scrubbers, Cleveland, Ohio. September 1974. Phone No. (216) 252-4141.

7. Otto H. York Company, Inc. Bulletin 52, The Demister, Fairfield, NJ, 1981. Phone No. (201) 575-6960.

8. Lowenheim, F. A. Electroplating, McGraw-Hill Book Company, New York, NY, 1978.

9. Koch Egr. Company Bulletin FF-2, New Flexifiber Mist Eliminator, Wichita, KS, 1980. Phone No. (316) 832-5110.

10. Sheppard, Stanton, Ionizing Wet Scrubbers Control Plant Emissions, Mechanical Engineering Magazine, July 1985, pp. 72-75.

11. Emcotek Brochure, Rotary Atomizing Scrubber, Emcotek Co., Visalia, CA, 1985. Phone No. (209) 651-2000.

LEGAL CASE STUDIES AND COMPLIANCE STRATEGIES

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Good morning! The topic I have been assigned for today's session is "Legal Case Studies And Compliance Strategies." I thought it might be helpful to you to briefly review some legal case studies that specifically apply to electroplaters, and then briefly review some do's and dont's for electroplating operations in forming a compliance strategy.

I say "briefly" because I don't think you want to get into legal jargon, or any preaching about the penalties or criminal sanctions for non-compliance. What I would rather do is try to give you some general guidelines for preventive medicine, in the hope that you'll know better how to avoid non-compliance problems, and also how to anticipate them and know what to do when they happen.

Let's start with a recent decision of the United States District Court for the District of Connecticut, named Connecticut Fund for the Environment v. Job Plating Company, decided September 17, 1985. This was a case in which Job Plating had filed non-complying Discharge Monitoring Reports during the period May, 1978 through November, 1983, pursuant to an NPDES permit issued in 1976. As was customary at that time, the NPDES permit was reissued in March, 1978. Apparently, the company began filing non-complying DMRs two months after its NPDES permit was reissued. Plaintiff served notice of intent to enforce the Clean Water Act and sue on the violations in September, 1983.

But there was one interesting feature about the Plaintiff in this case. The Plaintiff was not a government agency. It wasn't USEPA. It wasn't the Connecticut Department of Environmental Protection. It wasn't the Connecticut Attorney General.

The Plaintiff was the Connecticut Fund for the Environment--a public interest group. Neither USEPA nor Connecticut DEP had filed any action against Job Plating as of November, 1983, the time at which Connecticut Fund for the Environment sued Job Plating.

A little later, Connecticut DEP did sue Job Plating--4 months after the public interest group did. The state suit asked for an engineering report and the installation of approved wastewater treatment facilities. That suit was resolved, with no penalties assessed against Job Plating.

However, Connecticut Fund for the Environment didn't want an engineering report. It asked for something known in the law as summary judgment. Summary judgment is an early pre-trial motion that asks the Court to declare for the moving party that, based on the evidence as it is known at that time, there is no genuine issue as to any material fact and that the moving party is entitled to judgment as a matter of law. A motion for summary judgment says to the Court: "There is nothing for the jury to decide, Your Honor. The law is such that Your Honor can decide that we are entitled to judgment as a matter of law, based on the facts as they exist now."

Now, what evidence do you suppose Plaintiff used to try to establish that it was entitled to summary judgment? Job Plating's DMRs! The DMRs--properly signed and certified by Job Plating--were the evidence upon which Plaintiff contended that no genuine issue of material fact existed as to the violations, and that Plaintiff was entitled to judgment as a matter of law. "Judgment" meant that the Court should find Job Plating guilty of each violation and assess the statutory penalty--for example, $25,000 per day x 174 days.

Job Plating raised 5 defenses: the statute of limitations; that the Water Act prohibits retrospective relief in citizen's suits; that Connecticut DEP had primary jurisdiction of the suit; that the Court did not have jurisdiction because DEP was diligently prosecuting its own action; and that Job Plating's NPDES permit, which of course the DMRs showed violations of, was improperly issued. The

Court denied all these defenses, and granted summary judgment for Connecticut Fund for the Environment.

Job Plating did get a break, though. The Court granted Plaintiff's Motion for Summary Judgment, but it did not immediately assess penalties. It ordered instead that the parties reach a settlement agreement by a certain date as a result of the Court's ruling, or, failing that, to prepare draft final orders for the Court to sign. You can imagine the pressure that Job Plating is under now to reach a settlement with Plaintiff on fines and penalties. The settlement will have to be enough to induce Plaintiff not to execute on the Summary Judgment it was granted. The Court is free to levy fines and penalties up to the statutory maximum in satisfaction of the judgment--$25,000 per day.

A second case study comes not from reported legal decisions, but from personal experience. I once handled an electroplating case in Illinois that resembled Job Plating's situation. The company called in mid-1979 to advise that the Illinois Attorney General had instituted a civil enforcement action against the company before the Illinois Pollution Control Board. All cases are serious, particularly enforcement cases; but we regarded this one as a straightforward enforcement case and we thought we had it settled late that year--until another call came in from the company, which I will never forget. The Operations Manager called to advise that the wastewater treatment plant operator had told him that the DMRs showing non-compliance for the past five years had been consistently and regularly falsified.

We knew then that this case was far from over. First, we disclosed to the Illinois Attorney General, in person and through the company president, what the wastewater treatment operator had said. Then we were faced with a dilemma: If a criminal action against the company individuals were filed, the company officers would likely blame the wastewater treatment plant operator; and the treatment plant operator would likely contend that the company asked him to do it or knew that he was doing it. How could we represent both sides of the defense? We couldn't. We had to represent the company and its officers, and tell the plant operator to retain his own counsel. He did, reportedly at company expense.

Still, we thought we might have settled at least the civil case in early 1980 with an independent engineering report, a compliance plan, and a commitment to control equipment, coupled with efforts to tie into the POTW. But then on April 22, 1980, 10 years after Earth Day, came an 84-count indictment filed in Circuit Court by the Illinois Attorney General. It asked for criminal penalties against the company, and against each of the corporate officers, who were alleged to be high managerial agents of the company under the Illinois Environmental Protection Act. "High managerial agents" were those who knew or should have known of such corporate action as regularly falsifying DMRs over a 5-year period.

We finally did settle the case--on November 6, 1980, with a Plea Agreement as to all 84 counts. The company paid a penalty that was more substantial in 1980 than it would be now. And the company finally was relieved of the burden of truly intense discovery and motion work, and the most ornery government attorney I have ever opposed anywhere, that it had borne for almost two years. One of the best results of all for the company was that it finally was received into the POTW--no small feat in a small town in which the city fathers wanted nothing to do with what they perceived in the newspapers as known criminals.

Let's consider now what these cases may mean for us. Do you see any emerging patterns that may be helpful to you?

Let me offer some possibilities:

1. Don't falsify DMRs, and don't allow anyone in your company to do it. Self-reporting is at the heart of environmental law in this country, just as it is in tax law. To intentionally violate state environmental reporting law is to immediately incur criminal exposure to your company, your officers, and to you. There should be a company policy or compliance manual in effect that

prohibits an employee from any negligence or intentional distortion of environmental reporting law, and subjects him to immediate discharge for violation of the company policy.

2. Have the person directly in charge of compliance report directly to the company president. The compliance manager, or even the wastewater treatment plant operator, should have at least a "dotted line" to the company president. You don't want any bad news about compliance to reach you in diluted form because of faulty translation up through company ranks, or because of turf protecting in and around the corporate ladder.

3. Don't ignore a compliance problem, or assume that it will go away or solve itself. If your people are reporting problems, put yourself in the place of the Court in the Job Plating case. He concluded that non-complying DMRs entitled plaintiffs--a public interest group--to summary judgment. Connecticut DEP was never even involved in the case until after the public interest group filed suit, which was five years after the reported violations began. How will it serve your company, from the standpoint of preventive medicine, to think that your company might do better in court than Job Plating? To all those companies who say "they can't do that to us," consider what Lord Cromwell said to his opponent before the War of the Roses began: "Consider, in the name of Christ, that you might be mistaken."

4. If you are in doubt about what to do, get an independent expert; get an environmental lawyer. No one

likes legal fees or experts' fees. But if your people are describing a compliance problem that they can't solve or won't go away, you may need an independent technical opinion. Good environmental lawyers know who to recommend to you, if your plant people don't already know someone.

By the same token, if your problem is with an interpretation of the law, rather than technical compliance, get an environmental lawyer to lay out your legal options. Depending on the state in which you are located, they could include the following:

a) Permit Appeal. A legal appeal to modify your permit limits.

b) Site-specific Rulemaking. Changing the law to give you and you alone certain relief.

c) Statewide Rulemaking. Initiating a proceeding to change the state regulation that you violate.

d) Trade Association Rulemaking. A legal proceeding initiated in Washington, by you or the trade association of which you are a member, to change the USEPA's regulation or policy that affects you.

e) Enforcement Action. If suit is imminent, you may be well advised to litigate your legal defenses after you are sued, depending on their strength. Job Plating lost on all its defenses--but what did you think of those defenses when I described them for you? Desperate, weren't they?

That's because they were too late. What if Job Plating's defense had been this: The company identified a compliance problem in 1978, four months after its first noncomplying DMR. Its independent expert detected a problem in the process, as well as in the river intake water; and a further problem in the way the State sampled the effluent, based on split samples and the wording of the regulations. As a result, the company filed for a variance in 1979, for more time to study the situation and temporary immunity in the interim. The variance was granted in part in 1981, and the partial denial was appealed and is still pending. Now comes Connecticut Fund for the Environment with its Motion for Summary Judgment. You will resist it, will you not? Because you have built your case and your defenses in advance, by addressing the problem.

I think you would also agree that if you were the judge, and a company came before you after five years of noncomplying DMRs, now contending that its NPDES permit was wrongly issued nine years ago, you would know the look of a loser when you saw one.

f) Doing Nothing. You may conclude, on advice of your experts or counsel, that your company is in legal compliance; that you should do nothing; and that risk of suit is remote. Get a written opinion from counsel that this is the

> case. He may be right or wrong, but you will sleep better knowing that you addressed the problem, fully examined it, and reached the most informed conclusion you could. If things go badly down the road in litigation, you and your company will do well in your deposition when you testify that you saw the problem early and resolved it as best you could with professional advice.

Enforcement authorities generally don't file criminal actions against companies with whom they disagree on a matter of technical or legal judgment--even if the company somehow turns out to be wrong. Changing the law, or interpreting the law, and selling that interpretation to regulators, is what we do every day. But defying or ignoring the law is what angers the agencies, and rightly so.

Thank you for your time with me this morning. I have enjoyed being with you.

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HAZARDOUS WASTE REMEDIAL ACTION AND CASE STUDIES

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Introduction

Groundwater contamination assessment and clean-up has become a high priority on the agenda of environmental protection. The enactment of federal Superfund legislation has been followed by activity on the state and local levels to address contaminated sites not in the scope of federal cleanup efforts. Guidelines for development and implementation of remedial action at hazardous waste sites have been incorporated as part of the National Contingency Plan (NCP) which provides procedures and protocols for all cleanup activities associated with federal Superfund sites. The purpose of the NCP is to establish standardized methods for hazardous waste site activities to ensure that the cleanup activities deal adequately with issues of environmental protection, cost effectiveness and technical feasibility of applied treatment technologies, and protection of the health and safety of site workers and the general public. The NCP concepts have been largely adopted by State Agencies for use in non-Superfund site cleanup activities such as industrial groundwater contamination studies.

The operation of electroplating and surface finishing facilities has, in some cases, resulted in releases of hazardous materials such as degreasing solvents and metal and cyanide salts to the groundwater. To illustrate the process of investigation and cleanup typically applied in these cases, the NCP remedial action process will be outined followed by the presentation of case studies describing remedial actions undertaken at two facilities in the electroplating and surface finishing industry.

The National Contingency Plan

The NCP encompasses all hazardous waste site activities, from site discovery and notification, immediate waste removal activities, and long term remedial action activities. The discussion to follow will be restricted to remedial action, the primary focus of the case studies described herein.

A remedial action encompasses site investigations, data evaluation, selection of methods for containment, collection, treatment and disposal of hazardous contaminants, and design and implementation of the selected remedial methods. These steps are incorporated in the NCP, termed the Remedial Investigation/Feasibility Study (RI/FS), a six-stage process (Refer to Table 1).

Problem Assessment

A detailed site reconnaissance is conducted to identify site characteristics of significance, such as topography, visible signs of contaminants, and contaminant receptors such as surface water and proximity of resident populations. A retrospective site history is prepared to provide information on hazardous material use and disposal practices, and occurrence of onsite releases of hazardous materials. An overall plan is developed to define a scope of work and provide health and safety protocols for on-site activities.

Field Investigation

Sampling and analysis of environmental media (i.e. soil, groundwater, surface water, air) is conducted to identify the type and extent of contaminants. The field investigation may include screening techniques such as geophysical surveys (e.g. ground penetrating radar, seismic refraction) to provide preliminary information on contaminant distribution to aid in the planning of subsequent sampling activity. Preliminary screening is particularly useful if groundwater monitoring wells are to be installed to maximize the effectiveness of well placement, which can be a costly undertaking. The scope of the sampling and analysis effort will depend upon a number of factors including the size of the site, the number of potential contaminant sources, and the complexity of the hydrogeological conditions.

Data Interpretation

The data collected during the field investigation is analyzed to identify contaminant sources and map the distribution of individual contaminants. Contaminant distribution and hydrogeological data such as the rate and direction of groundwater flow is used to predict significant pathways of contaminant transport and probable receptors of the contaminants. Evaluation of the initial data base may indicate that additional sampling locations are required to adequately characterize the site and impacted receptors.

Risk Assessment

The potential impact of contaminants identified in previous stages is evaluated by the risk assessment process. The effect of contaminants on the human population and the environment is assessed, with mechanisms of exposure and potential exposure levels investigated relative to the toxicity of individual identified contaminants. The criteria used to evaluate the impact of contaminant concentrations includes established standards such as drinking water standards and surface water discharge limits. Additional criteria may be developed from literature sources, particularly in the case of contaminants that do not fall under current standards. A major problem with conducting risk assessments is the lack of a standardized methodology. Site conditions and the requirements of state and local agencies will affect the content and extent of a risk assessment.

Feasibility Study

The feasibility study is a process of selecting the best method of mitigating the effects of contaminants identified at the site. The selection process is applied to all aspects of the remedial action, from containment or collection of contaminated air, water, wastes, or soil, to treatment or fixation of contaminants, and disposal of contaminants on or off-site. The range of environmental media (soil, water, etc.) affected and their levels of contamination will influence the number of alternatives to be considered.

Alternatives are judged on the basis of several criteria. Technical feasibility, level of risk to public health and the environment, cost, and regulatory requirements are all considered to select a final remedial action plan. Those alternatives meeting the prescribed criteria are then subject to public review and comment. A final remedial action plan is then selected that will address the cleanup both from a technical and a political standpoint.

Design and Implementation

The remedial action plan enters the conceptual design phase where it is subject to regulatory review. Implementation of the plan then follows, with the completion of final engineering design activities to initiate the preparation of construction documents (i.e. drawings and specifications) and procurement of applicable permits.

The preceding development of the elements of a NCP-based RI/FS illustrate the procedure as implemented on the Federal Superfund level. Many of the same elements are incorporated into state-supervised cleanup efforts, as will be demonstrated in the following case studies.

CASE STUDY 1

Introduction

Site 1 involves the release of wastewater from a facility engaged in electroplating of electronic components. The facility is located on a six-acre site in an area of light industry bordering on a residential area of condominiums and single family dwellings.

Problems at the facility including wastewater discharge violations and visible signs of wastewater leakage into the soil were the subjects of inspections by the municipal sewer authority and the local Board of Health in 1980 and 1981. In 1983, suspected soil contamination from a leaking wastewater conveyance pipe was verified by soil testing conducted by the owner of the site, which indicated contamination of the soil with metals, cyanides, acids, and volatile organic compounds (VOCs) such as 1,1,1-trichloroethane. The state environmental agency hazardous waste division was notified of the evidence of a release to the environment, and the agency ordered a complete site assessment to be conducted. The site assessment activities were initiated in January, 1984.

Inside the facility, corrosion in the wastewater conveyance trench system was discovered to have allowed leakage of wastewater to the soil below. Contaminated soil beneath the trenches was excavated and disposed as a hazardous waste along with the corroded concrete lining the trenches. This action was taken outside the framework of a Remedial Investigation/Feasibility Study, an action agreed upon by the owner and the regulating agency as a positive and expedient resolution of the problem. The action was taken at the request of the owner to allow an on-going renovation of the building interior to proceed on schedule.

Site History

A site history was compiled to identify past and present chemical usage and waste handling and disposal practices. Existing analytical results on samples of soil and groundwater, wastewater discharge monitoring reports, hazardous waste hauling invoices, and raw materials purchases were incorporated, rumors were heard of drums containing hazardous waste being buried on-site and other information which would be useful in planning a site sampling and analysis plan, as well as providing a preliminary basis for designing a site safety plan.

Field Investigation Activities

Geophysical survey techniques were employed on the site prior to additional sampling efforts in order to provide information about the subsurface geology, the depth to water table, contaminant distribution, and the presence of buried waste drums. Seismic refraction, electrical resistivity, electromagnetic induction, and ground penetrating radar were used to study the site. The data gathered from the geophysical surveys was used to plan the construction and installation of groundwater monitoring wells and to help locate the wells in areas of probable contaminant occurrence. No evidence of buried waste drums was found and the issue of buried drums was of no further concern.

The field investigation included installation of nine groundwater monitoring wells including one well intended as a background well, located upgradient of the site groundwater flow and at a distance of 170 feet from the facility (Refer to Figure 1). Hydrogeological observations were made to determine soil permeability and other groundwater flow characteristics. Soil and groundwater samples were collected from the well installations and analyzed for a range of test parameters based on the site history. Table 2 lists the maximum observed levels of major contaminants found in groundwater sampled from the monitoring wells.

Data Interpretation/Risk Assessment

The major contaminant source was found to be leaking underground wastewater collection sumps, with lesser contributions from other sources such as leaking wastewater conveyance pipes and trenches. The wastewater was introduced into a fine sand and silt material that was found to be the predominant soil type above bedrock. The fine grained material limited movement of the contaminants in both the horizontal and vertical directions. It was estimated that very limited off-site migration of contaminants could have taken place, given the calculated rates of travel (approximately four feet per year) and the 20 year period over which the facility had been operating and using chemicals. Movement of contaminants through the uderlying aquifer was the only avenue of migration of contaminants away from the site, since the contaminants were not located near the surface and could not be picked up by surface run-off. The nearest receptors in the path of groundwater flow from the site were a group of private water supply wells located approximately 1,700 feet downgradient of the site. The major risk associated with the contamination at Site 1 was degradation of the aquifer water quality that could render the local water supply wells unusable. The impact of the contaminants on the aquifer can be seen by comparison of the observed contaminant levels with the state groundwater quality standards, also listed in Table 2.

Groundwater Recovery and Disposal

Selection of remedial action alternatives began with the decision to recover contaminated groundwater from the aquifer for treatment. The alternatives for groundwater recovery included deep wells with submersible pumps and well point systems for use at shallow depths. Further information was provided in this area by the construction at the site of a groundwater recovery well which was used to perform a pump test to evaluate the response of the aquifer to extended pumping. The results of this test indicated that deep wells would be more efficient in collecting groundwater on the site than a shalllow well point system. A total of four wells would be required to effectively contain the contaminated groundwater and collect it for treatment.

Before considering alternatives for treatment of the recovered groundwater, it was useful to explore the range of possibilities for disposal of the treated groundwater, since the method of disposal would have an effect on the level of treatment required. The three alternatives for disposal of treated groundwater were: use as process water, with final treatment and disposal to the municipal sewerage system; discharge to surface water; and on-site recharge of the aquifer.

Process use and discharge to the sewerage system was attractive from the standpoint of decreased water supply costs and the relatively less rigorous discharge standards imposed by the sewer authority, but was limited by the process water quality requirements and the limited volume that could be recycled versus the amount of groundwater to be recovered for treatment. Discharge to surface water required the most exacting treatment to meet stringent aquatic toxicity standards.

On-site recharge was selected as the most feasible method of disposal. Through proper placement of recovery wells and the recharge system, the treated groundwater could be recycled in a closed loop system, which offered the possibility of soil flushing to extract contaminants which might otherwise be left in the soil. The closed loop concept was also favored by the regulatory agency and would allow initial discharge of treated groundwater at levels exceeding the groundwater quality standards, provided that groundwater quality standards would be met at some point before system shutdown.

Groundwater Treatment

Alternatives for groundwater treatment were considered in three parts; metals, VOCs, and anions such as fluoride and sulfate. Alternatives for metal removal included chemical precipitation followed by conventional sedimentation and granular filtration, and chemical precipitation followed by ultrafiltration. The ultrafiltration alternative was chosen because an existing on-site wastewater pretreatment system utilizing ultrafiltration technology became available for use in groundwater treatment. This approach afforded the advantages of cost effectiveness and ease of implementation while providing acceptable metals removal. A treatability study was performed on a representative sample of contaminated groundwater to assess system performances and effluent quality results. Using lime addition to a pH of 9.5 s.u., the following results were obtained:

Metal	Influent, mg/L	Effluent, mg/L	Groundwater Quality Standard, mg/L
Nickel	20	0.1	0.63
Copper	18	0.1	1.0
Cadmium	0.06	0.003	0.01

Air stripping and granular activated carbon (GAC) were considered as alternative treatment technologies for VOC removal. Both treatment methods were feasible from the standpoint of being able to achieve the desired VOC removals. Operationally, GAC required periodic regeneration of the carbon bed, requiring on-site regeneration equipment or hauling the carbon to an off-site facility. The potential for VOC breakthrough as the carbon approaches its capacity for adsorption requires careful monitoring of the effluent. Air stripping however, provides relatively constant removal performance with minor operation and maintenance requirements, and no associated residual waste disposal costs. For these reasons, air stripping was chosen for VOC removal at Site 1.

Removal of the anionic components of the groundwater, sulfate, fluoride, chloride, and nitrate, required the likely use of reverse osmosis or ion-exchange, at significant increases in treatment system equipment costs and operating and maintenance requirements. Estimation of the dilution effects that would be achieved during the groundwater recovery/recharge cycle however, indicated that without treatment, the anions would be reduced to groundwater quality standard levels or below, and that no adverse effects on groundwater quality would occur. In this case, the "no action" alternative was seen to be cost-effective and environmentally acceptable.

Remedial Action Plan Design

The final remedial action plan consisted of four major elements: groundwater recovery wells, chemical precipitation/ultrafiltration, air stripping, and treated groundwater recharge. Following approval of the conceptual design by the regulating agency and public review through the mechanism of the groundwater discharge permit process, implementation of the remedial action plan was initiated.

Final design parameters for the groundwater recovery wells and the recharge system were developed from previously obtained pump test data and permeability testing conducted on-site. Groundwater recovery was achieved with four wells extending into bedrock with a combined design pumping rate of 80 gallons per minute (gpm). Treated groundwater would be recharged to the site through a leaching trench with an area of 3,600 square feet, 420 feet in length.

The air stripper design was completed using data obtained during a pilot test conducted on-site. The final air stripping design specified a 4 foot diameter stripping tower with 11 feet of packed height, with recirculation of the groundwater through the tower for multiple-pass treatment capability. The maximum volume/volume air to water ratio was 450:1 at 80 gpm. The overall design removal efficiency was 99.91%.

CASE STUDY 2

Site Conditions

The site described in Case Study 2 occupies an area of 270 acres, 100 of which are developed with buildings, parking and storage areas, etc. The facility operations include printed wiring board production. A number of VOC spills occurred in the developed area, beginning about 1957. Trichloroethylene was the principal contaminant found at the site. VOC contamination in the groundwater was measured at levels as high as 250,000 parts per billion (ppb) in an area of 3 to 4 acres, with a total area of about 60 acres exhibiting VOC levels of 100 ppb or greater.

The overburden soil is separated from bedrock by a relatively impermeable layer of glacial till, forming two aquifer systems. Leakage of VOCs into the lower bedrock aquifer was influenced by the presence of industrial water supply wells at the site, causing a downward flow component of the groundwater from the overburden to the bedrock.

Remedial Action

Remedial action at the site was concerned with preventing off-site migration of VOCs and removal of VOC from the groundwater. As in Case Study 1, groundwater pumping and treatment was chosen as the preferred remedial action. Disposal alternatives for treated groundwater included process use, direct discharge to the municipal sewerage system, and on-site recharge. The presence of naturally occurring iron concentrations of up to 35 parts per million (ppm) in the groundwater would require iron removal as part of the treatment system if the process reuse alternative was selected. Discharge to the municipal sewer was selected as the most cost-effective alternative.

The groundwater recovery system was designed to withdraw groundwater from the overburden and bedrock aquifers with two separate well systems to prevent further downward migration of VOC contaminated groundwater into the bedrock aquifer. It was determined that such migration would increase the time required to complete groundwater renovation. The overburden recovery system was designed as a shallow well point system composed of 24 well points. An existing deep well was selected for groundwater recovery from the bedrock. The total design withdrawal rate of groundwater from the well systems is 160 gpm.

As in Case Study 1, air stripping was selected as the treatment alternative for VOC removal. Final design of the air stripper was based on a pilot study conducted at the site. The desired VOC effluent concentration for discharge of treated groundwater to the municipal sewer was 50 ppb, total VOCs. The specified system, for a design flow of 160 gpm, was a two tower system in series. Each tower was 3 feet in diameter with a packed height of 24 feet and a removal efficiency for trichloroethylene of 99.5 per cent per tower at a volume/volume air to water ratio of 100:1.

Summary

Two remedial action case studies have been presented that illustrate the remedial action process as conducted by site owners. In both cases, the remedial action process, from site investigation through implementation was conducted over a period of approximately 2-1/2 years. Investigation of the site hydrogeology and contaminant distribution accounts for a large proportion of project duration, but it is time well spent. Complexity is the rule rather than the exception when describing site hydrogeology, and insufficient data will inevitably result in inadequate design and excessive cost impacts. The stepwise approach to remedial action as described herein is intended to ensure that both the technical and economic aspects of a project are properly addressed so that a successful result is achieved.

TABLE 1

ELEMENTS OF A REMEDIAL INVESTIGATION/FEASIBILITY STUDY

1. Problem Assessment	- detailed site reconnaissance
	- site history
	- overall plan design
2. Field Investigation	- define scope
	- conduct investigation
3. Data Interpretation	- integrate data
	- identify contaminant sources, pathways, potential receptors
4. Risk Assessment	- toxicity of contaminants
	- mechanisms of exposure, potential exposure levels
	- potential impacts
5. Feasibility Study	- identify possible remedial actions
	- screen on basis of technical feasibility, level of risk, cost, and regulatory requirements
	- presentation for public review
6. Design and Implementation	- conceptual design for agency review
	- implementation, final engineering design, construction documents, and permits

Reference: Federal Register, November 20, 1985, P. 47912

TABLE 2

CASE STUDY I - CONTAMINANTS IN GROUNDWATER

Contaminant	Maximum Observed Level (PPM)	Groundwater Standard (PPM)
Cadmium	1.9	0.01
Copper	530	1.0
Nickel	120	0.63*
Sulfate	11,000	250
Chloride	2,190	250
Nitrate Nitrogen	149	10
Fluoride	40	2.4
Total Cyanide	3.2	0.2*
1,1,1-trichloroethane	91	0.14*
Trichloroethylene	6.6	0.07*
Tetrachloroethylene	2.6	0.02*

* Based on US EPA, Water Quality Criteria for Human Health (1980).

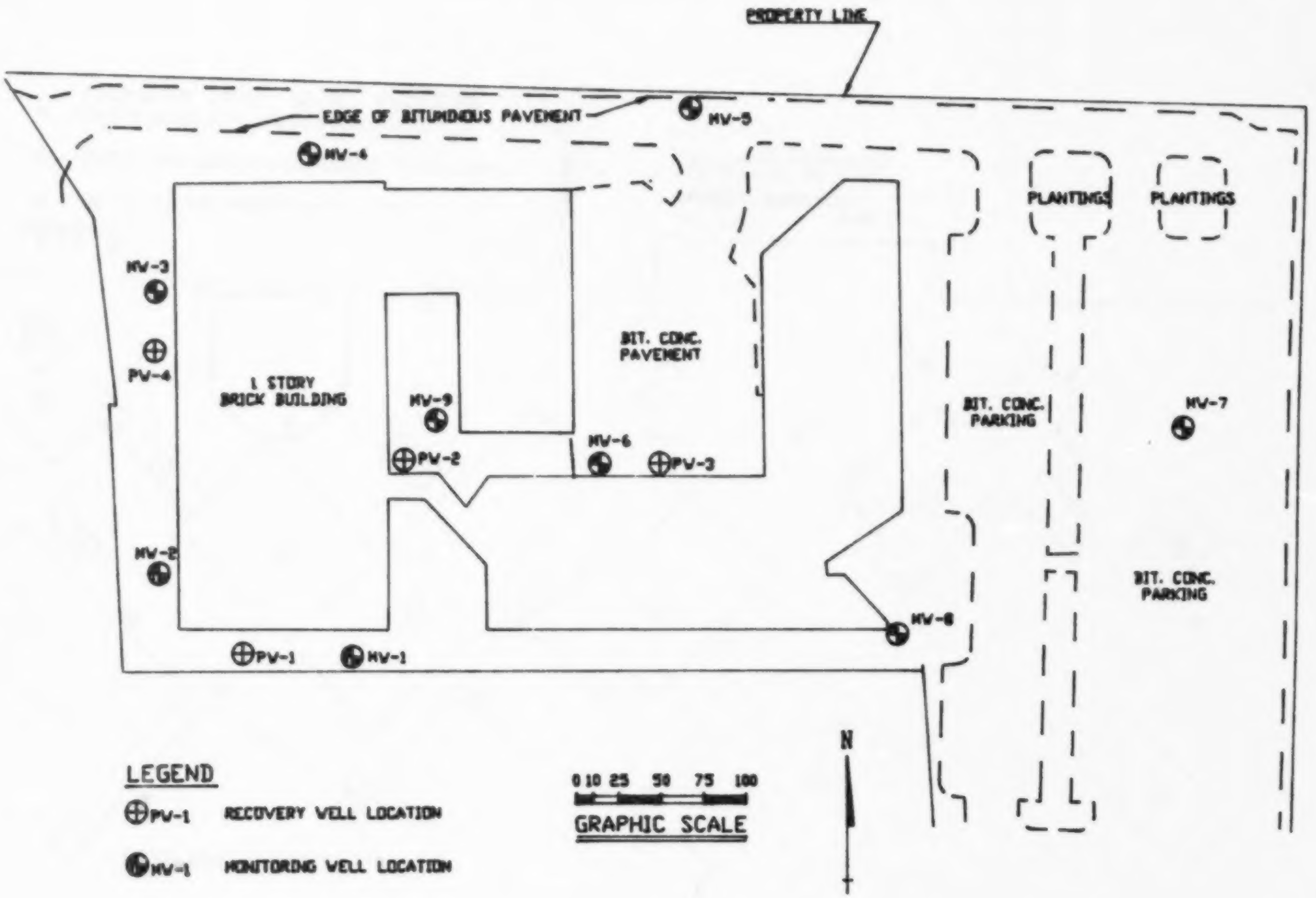
PROPERTY LINE
EDGE OF BITUMINOUS PAVEMENT
MW-5
MW-4
MW-3
RW-4
1 STORY
BRICK BUILDING
MW-9
RW-2
BIT. CONC.
PAVEMENT
MW-6
RW-3
MW-2
RW-1
MW-1
MW-8
PLANTINGS
PLANTINGS
BIT. CONC.
PARKING
MW-7
BIT. CONC.
PARKING
LEGEND
RW-1 RECOVERY WELL LOCATION
MW-1 MONITORING WELL LOCATION
0 10 25 50 75 100
GRAPHIC SCALE
N

FIGURE 1. SITE PLAN CASE STUDY 1

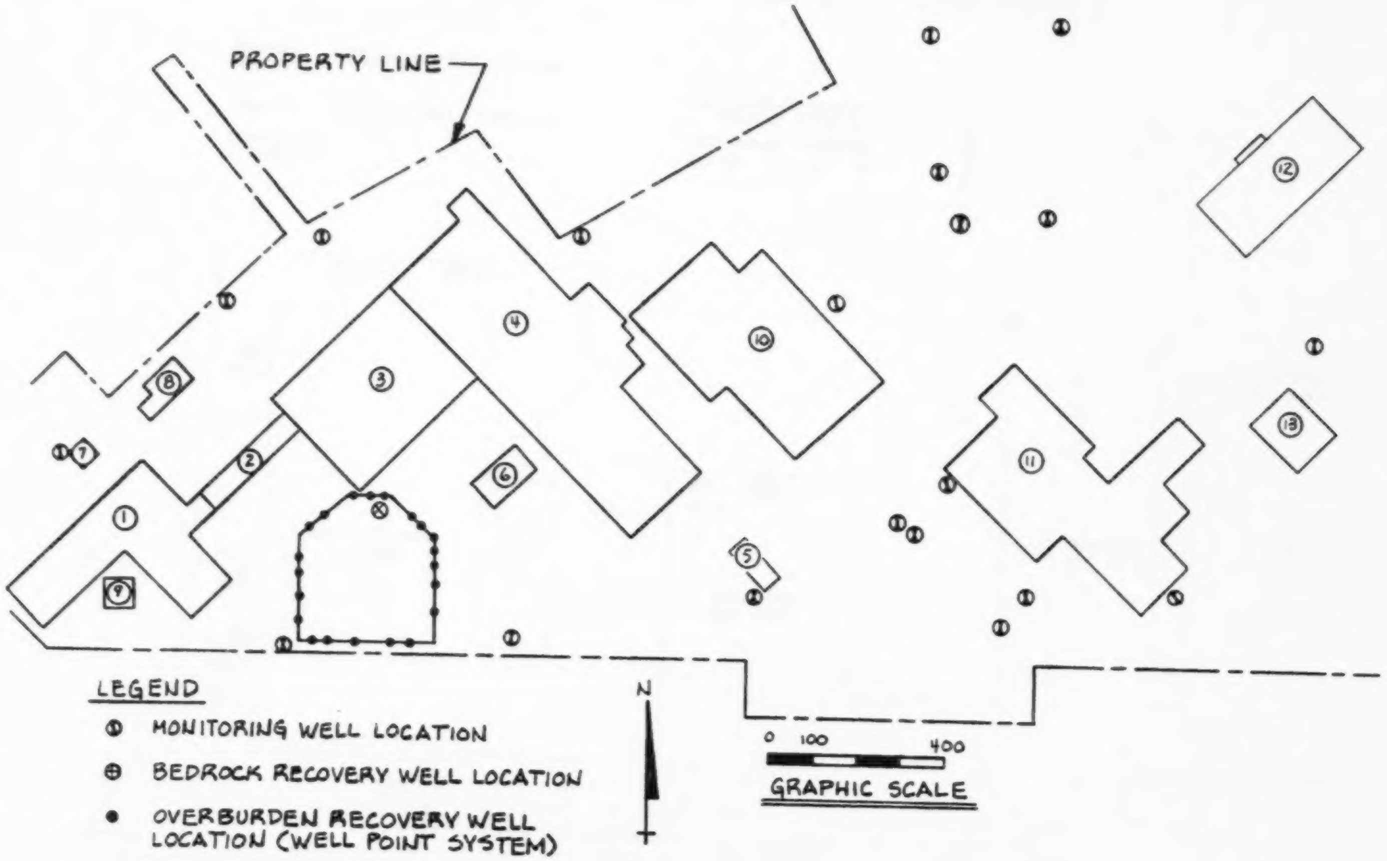
PROPERTY LINE
①
②
③
④
⑤
⑥
⑦
⑧
⑨
⑩
⑪
⑫
⑬
LEGEND
MONITORING WELL LOCATION
BEDROCK RECOVERY WELL LOCATION
OVERBURDEN RECOVERY WELL LOCATION (WELL POINT SYSTEM)
N
0
100
400
GRAPHIC SCALE

FIGURE 2. SITE PLAN CASE STUDY 2

COMPARATIVE STUDY OF THE USE OF PLASTIC MEDIA BLASTING FOR PAINT STRIPPING

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Introduction

Paint removal operations can be major generators of air, water, and solid waste pollution. There are two traditional methods used for industrial paint removal operations--sandblasting and chemical stripping. Over 60,000 tons per year of methylene chloride is used as a chemical stripping agent resulting in air, water, and solid waste pollution. In addition, countless tons of metal contaminated sand from sandblast stripping operations must be disposed of in an environmentally safe manner. Therefore, the unique method of plastic media blasting (PMB) for paint removal promises to significantly reduce air, water, and solid waste pollution from paint stripping operations.

In early 1985, the U.S. Army and the U.S. Environmental Protection Agency embarked upon a joint effort to identify major sources of multimedia pollution from selected Army maintenance operations. The second objective was to recommend solutions to the identified pollution problems and evaluate their potential to reduce pollution discharges. The Army facility selected for the initial evaluation program was the Sacramento Army Depot, California. The two major hazardous pollutant sources identified were chemical stripping and the sandblasting paint removal operations. Plastic media blasting for paint removal was recommended as a replacement for sandblasting and chemical stripping. A joint research project was initiated with the U.S. Army Toxic and Hazardous Materials Agency to compare plastic media blasting with sandblasting and solvent chemical stripping. The sandblasting and the plastic media blasting operations were evaluated at the Sacramento Army Depot. The chemical stripping operation was evaluated at the McClellan Air Force Base, California, Air Logistics Center.

This paper presents the technical, economic, and environmental findings of the program that evaluates and compares the three paint removal processes. The paper addresses three areas: the quality of the finished product, the speed of removal, and the environmental impact of each process.

Background

The use of organic chemicals or sandblasting are the most common methods for removing paint from metal or composite structures. Typical military specification strippers contain up to 85 percent methylene chloride, a designated hazardous pollutant. Other organics which can be found in these strippers include methyl ethyl ketones (MEK) and phenols. These chemicals, when used in industrial stripping operations, result in both air and water pollution. The increasing restrictions on the discharge of these chemicals and other contaminated wastes by the U.S. EPA and the State environmental agencies will make future discharge and disposal difficult and more expensive.

Many institutions have been researching substitute methods for removing old or damaged paint. Methods under investigation include laser light, flash lamps, and high pressure CO_2 pellets--another form of blasting. The methods in most common usage, however, are chemical stripping and sandblasting. Both of these methods, however, have inherent problems. Sandblasting can be aggressive to softer metals and composites. Chemicals result in large volumes of contaminated rinse water and sludges.

Plastic media blasting (PMB) is a unique variation of the sandblasting process which uses plastic beads rather than silica sand. Similar to sandblasting, the media impacts upon the surface and attacks the paint covering the substrate. However, due to the hardness of the plastic beads, approximately 3 to 5 Mohs, it is non-abrasive to the metal substrate, which typically has surface hardness greater than 6 Mohs. Sand has a Mohs hardness of approximately 7. The relatively low Mohs hardness of the plastic beads permits PMB to be used on surfaces and in areas which cannot be processed by sandblasting or chemicals and, therefore, has a significant advantage over other stripping techniques. A disadvantage, however, is that plastic media blasting will not remove rust, since the beads are softer than rust.

Evaluation Approach

The PMB evaluation program was designed to address three areas: the quality of the surface finish, the speed of paint removal, and the environmental impact of the process compared to other stripping processes. The quality requirements of the surface finish were defined by military specifications, with surface quality evaluations completed by facility technicians. The stripping speed and environmental impact evaluations were completed by using elapsed time and analytical results, respectively. The time determinations were nozzle-on elapsed times for PMB and sandblasting evaluations, and application, setting, and rinsing elapsed times for chemical stripping. The recorded elapsed times did not include unit preparation times, although sandblasting and chemical stripping would have increased unit processing times. Due to the aggressive nature of sandblasting and chemicals, hand sanding is normally required to process the interior of the electronic shelters of this evaluation. PMB can be used on the interior surfaces without causing damage. Hence, hand sanding was not required unless to remove rust. Also, PMB did not attack or affect rubber seals or gaskets, thus surface preparation was not required.

A total of 14 shelters of similar size and configuration were evaluated. They included three evaluated for chemical stripping, six for sandblasting, and five for PBM. Figure 1 shows a typical electronic shelter of the type used during the evaluation. The quantitative data collected during each evaluation run included total shelter surface area, stripping times, paint type, material used, and volume of waste generated.

Sandblasting

Sandblasting evaluations were conducted at the Sacramento Army Depot, California. A total of six shelter stripping operations were observed. Due to the abrasive effect of sand on the aluminum surface of the shelters and potential contamination of sand on electronics, only the outside of the shelters were sandblasted. The inside of the shelters were stripped by hand sanding. As shown in Table 1, the paint removal rates for sandblasting on the outside of each shelter ranged between 2.86 and 10.49 ft^2/min.* However, the inside removal rate averaged only 0.74 ft^2/min. Thus, the actual cleaning rate for sandblasted shelters for both inside and outside ranged between 1.8 and 5.6 ft^2/min. It should also be noted that inside stripping was incomplete and of minimal quality. As expected, multi-layered coatings required the greatest effort. As shown for units 3 and 5 in Table 1, which were coated with multi-layered camouflage paints, the paint removal effort was two to three times slower than for single coatings.

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*Readers more familiar with metric units may use the conversion table at the end of this paper.

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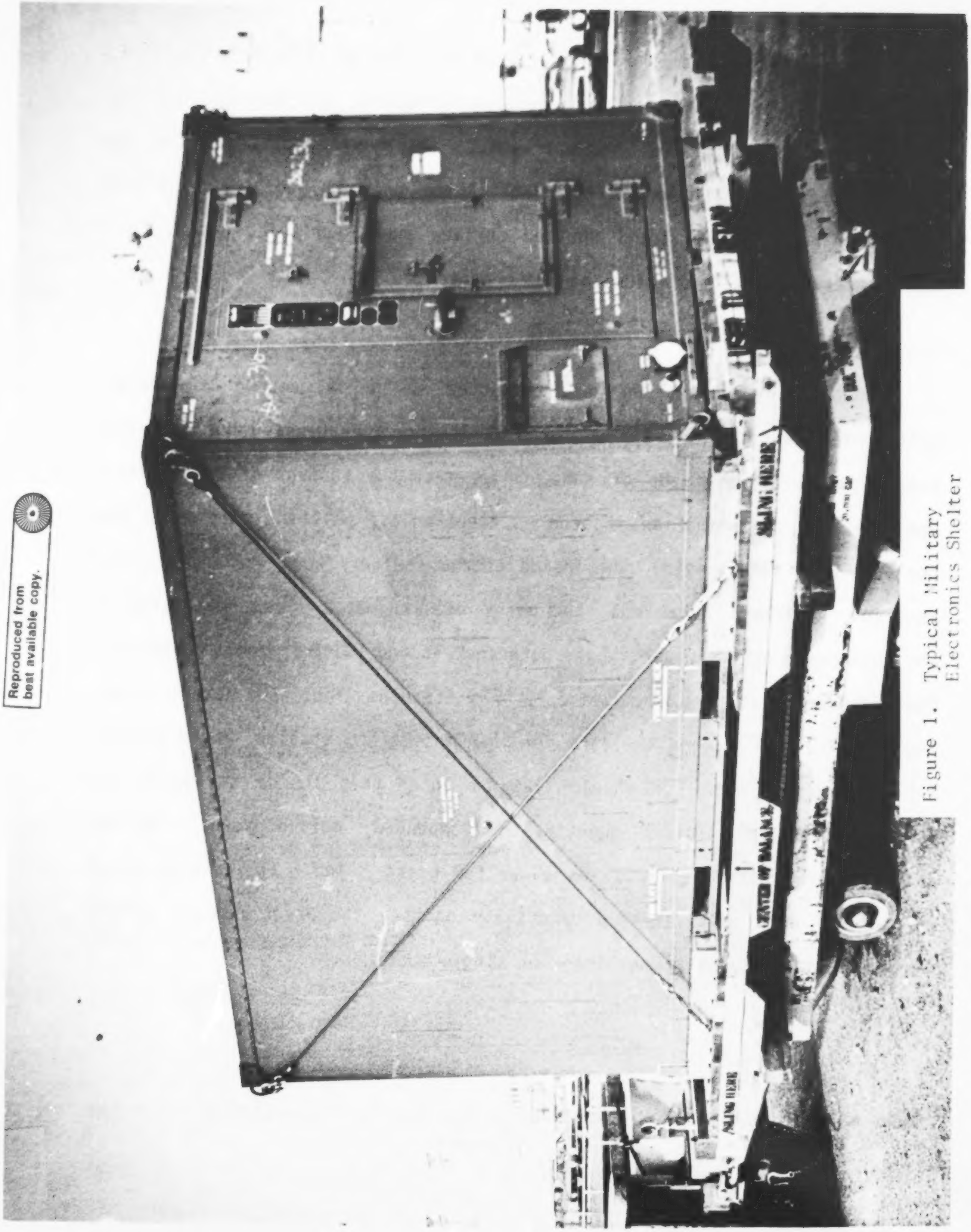

Figure 1. Typical Military Electronics Shelter

TABLE 1. SUMMARY OF SANDBLAST STRIPPING

Unit No.	Area Stripped (ft^2)		Stripping Time (min)		Rate (ft^2/min)		Estimated Stripping Rate (ft^2/min)	Sand Used (lb)	Material Rate (lb/ft^2)	Waste Rate (lb/ft^2)
	Outside	Inside	Outside	Inside	Outside	Inside				
1	189	71[a]	24.4	93[a]	7.74	0.76[a]	4.25	325.6	1.7	1.7
2	189	36[a]	25.0	50[a]	7.56	0.72[a]	4.14	333.3	1.8	1.8
3	189[c]	--	66	--	2.86	0.74[b]	1.8	880.0	4.7	4.7
4	249	--	33	--	7.54	0.74[b]	4.14	440.0	1.8	1.8
5	249[c]	--	67.3	--	3.70	0.74[b]	2.20	897.3	3.6	3.6
6	249	--	23.8	--	10.49	0.74[b]	5.60	317.6	1.3	1.3

[a] Real time data
[b] Estimated sand rate
[c] Multilayered

Chemical Stripping

Chemical stripping evaluations were conducted at the USAF Air Logistics Center, McClellan AFB, CA. One small and two medium size shelters were observed. Data similar to those taken during the sandblasting evaluations were collected. However, the total outside processing time included the sum of the chemical application, reaction, and rinse-down elapsed times. The stripper was primarily methylene chloride in a wax base to allow adherence to the unit surface. For certain difficult removal situations a supplementary phenolic stripper was used. Table 2 summarizes the results of the chemical stripping evaluations.

Chemical stripping was also determined to be a time-consuming process with equally large volumes of liquid waste. Also, due to the corrosive nature of the stripping chemical, only the outside was chemically stripped. Thus, the inside of each unit was stripped by hand sanding which, when combined with the outside stripping time, was less than the sandblasting rate. The waste generated as shown in Table 2 was approximately equivalent to that generated during sandblasting. The waste generation rate ranged between 1.7 and 3.3 gal. liquid waste per square foot of surface area. The waste volumes were determined by the thickness of the coating and its resistance to the chemical stripper. As shown for unit 3 in Table 2, the stripping rate was significantly less than for the larger units and, due to the additional stripper applications, the waste generation rate was significantly greater. Approximately 25 percent of the liquid waste generated required handling and disposal as a hazardous waste sludge.

TABLE 2. SUMMARY OF CHEMICAL STRIPPING

Unit No.	Area Stripped (ft^2)		Stripping Time (min)		Rate (ft^2/min)		Total Average (ft^2/min)	Chemical Used		Chemical Use Rate (lb/ft^2)	Waste Rate (gal./ft^2)
	Outside	Inside	Outside	Inside	Outside	Inside		(lb) Stripper[a]	(gal.) Water		
1	342	N/A	692	N/A	0.50	0.74[b]	0.62	194	1572	0.57	1.9
2	387	N/A	1345	N/A	0.30	0.74[b]	0.51	370	2636	0.96	1.7
3	180[c]	N/A	1126	N/A	0.17	0.74[b]	0.46	149	2336	0.83	3.3

[a] Includes all organics
[b] Estimated from sandblast results
[c] Supplementary phenolic stripper used

Plastic Media Blasting

Five shelters were processed at the Sacramento Army Depot using plastic media blasting (PMB). The units were of similar size and configuration of those evaluated for chemical stripping and sandblasting. However, unlike the chemical stripping and sandblasting operations, both the outside and inside of each shelter was stripped using PMB, thus eliminating the time-consuming hand sanding. The times determined for stripping those units, therefore, included both the inside and outside. In addition, since PMB had no effect on seals, gaskets, or surface preparation, masking was not required.

The plastic media was blasted at approximately 30 psi, which is lower than for sandblasting. Over the total evaluation program, a total of 450 lb of paint dust and media were discarded as waste. This represented 18 percent of the media charge. Table 3 summarizes the results of the PMB evaluation. Since hand sanding was not required, the inside cleaning rate was typically no greater than twice the outside cleaning rate. This difference can be attributed primarily to the limitations of the evaluation site. Unlike a dedicated PMB installation with bead retrieval apparatus and filters, the inside of each shelter was stripped without the aid of bead retrieval or ventilation to remove dust. Thus, periodic shutdown was required during the evaluation to permit bead retrieval and dust settling. The stripping rate for Shelter A (Table 3) was significantly less than those recorded for the remaining shelters in the series. A silica impregnated floor coating was used which required significantly greater effort to strip. The stripping rate for the remaining shelters reflected the relative paint thicknesses between the single coatings and the multilayered camouflage coatings.

TABLE 3. SUMMARY OF PMB PAINT REMOVAL

Shelter	Area (ft^2)			Stripping Time (min)			Cleaning Rate (ft^2/min)		Average Cleaning Rate (ft^2/min)	Plastic Media Usage Rate[a] (lb/ft^2)	Waste Material (lb)	Material Waste (lb/ft^2)
	In	Out	Total	In	Out	Total	In	Out				
A[b]	394	335	729	588	201	789	0.67	1.67	0.92	<0.18	<131	<0.18
B	178	168	346	82	139	221	2.17	1.21	1.57	<0.18	<62	<0.18
C	178	168	346	102	69	171	1.75	2.43	2.02	<0.18	<62	<0.18
D[b]	394	335	729	136	123	259	2.90	2.72	2.80	<0.18	<131	<0.18
E[b]	178	168	346	47	113	160	3.79	1.49	3.06	<0.18	<62	<0.18

[a] Estimated from total waste product generated over the evaluation program

[b] Multilayered camouflage enamel paint

Results and Discussion

The viability for industrial application of any paint stripping process is defined by its costs and the quality of the surface finish after stripping. Thus, the objective of this program was to determine the technical and economic factors that define the limits of the plastic media blasting (PMB) technique and compare them to those for sandblasting and chemical stripping. The results relied both upon the subjective judgements of quality control experts and on realtime data collected during stripping operations at two military maintenance facilities.

The surface quality after paint stripping was determined by quality control inspection based upon military specification surface requirements. Three techniques produced acceptable repainting surfaces, although of varying degrees of quality. The inside surfaces of the sandblasted and chemically stripped units were of minimum overall quality since hand sanding permits only partial removal of paint. The PMB units were determined to have the best overall surface quality. For PMB the surface quality of the inside was considered equivalent to the stripped outside surfaces. The stripping rate of PMB on simple flat metal (T2024 aluminum) surfaces was determined to be less than that for sandblasting, but greater than for chemical stripping. However, due to the complex surfaces inside the shelters, PMB was significantly faster (by a factor of three) on the interior surfaces when compared to hand sanding. Thus, based on the average stripping rate for each process, PMB was at least 30 percent faster than sandblasting and 65 percent faster than chemical stripping, since both require hand sanding of the interior surfaces.

Because sandblasting waste is not presently disposed of as a hazardous waste at the test site, PMB was determined to be marginally more expensive than sandblasting, but significantly less expensive than chemical stripping. As shown in Table 4, and based on an 82 percent recycle rate for PMB, the process cost for sandblasting was determined to be approximately \$0.35 per ft^2, with PMB and chemical stripping \$0.48 and \$2.58 per ft^2, respectively. By breaking down the respective cost element as in Table 4, it can be seen that the significant cost element for sandblasting, however, was labor at \$0.25 per ft^2. The materials costs were \$0.09 per ft^2 for high-grade sand, and subsequent waste disposal was less than \$0.01 per ft^2 stripped. The disposal rate for PMB was determined to be marginally higher than sandblasting due only to the designation of sandblast waste as non-hazardous. A change in the designation of sandblast waste would result in a waste disposal cost for sandblast in excess of \$0.13 per ft^2 and thus increase the total process cost for sandblasting to \$0.50/ft^2. Due to the efficiency of PMB in processing the inside of the shelters, thus eliminating time-consuming hand sanding, the actual labor rate for PMB was significantly lower than for the other processes.

Finally, the plastic media recycle rate as determined during this program was 82 percent. This was due primarily to the limitation of the experiment. Since the beads can be effectively classified and recycled at greater than 90 percent, it is therefore possible and probable that most operations would operate at a 90 to 95 percent recycle rate. Thus, the major cost item for PMB material cost at \$0.36 per ft^2, could be significantly lowered. At a 90 percent recycle rate, the material rate for PMB

TABLE 4. COMPARISON OF PAINT STRIPPING METHODS FROM DATA COLLECTED DURING EVALUATION

Paint Stripping Method	Average Stripping Rate (ft^2/min)		Material Use Rate (lb/ft^2)	Waste Generation Rate (lb/ft^2)	Estimated Labor Rate[a] (\$/ft^2)	Material Cost Rate (\$/ft^2)	Waste Disposal Rate (\$/ft^2)	Total Process Cost[b] (\$/ft^2)	Projected Process Cost[c] (\$/ft^2)
	Outside	Inside							
Sandblasting	6.64	0.74	2.4	2.4	0.25	<0.09	<0.01[d]	0.35	0.50
Chemical	0.32	0.74	0.8	2.3	0.65	1.80	0.13[e]	2.58	2.58
Plastic Media Blasting	2.26	1.9	<0.18	<0.18	0.10	0.36	0.01	0.47	0.31

[a] Labor rate estimated at \$10.00 per hour

[b] Based on collected data

[c] Based on added assumptions: (1) Sandblast waste treated as hazardous waste
(2) 90 percent bead recycle rate

[d] Disposed of at nonhazardous rate

[e] Approximately 25 percent of total liquid waste disposed of as hazardous waste

would be reduced by 55 percent to approximately \$0.20 lb/ft^2 and thus more economical than sandblasting or chemical stripping. The last column of Table 4 compares the process costs based on a 90 percent plastic media recycle rate.

Conclusions

The results of the evaluation program data for PMB indicate that PMB is only marginally more expensive than sandblast paint stripping. However, with only a minor increase in plastic media recycle rates, PMB will be less expensive to operate than sandblasting and has the benefit of lower disposal volumes.

The quality of the surface finish using PMB is superior to that using chemicals or sandblasting. PMB does not require masking, or result in surface etching or seal destruction. This permits significant time and long-term cost savings over other techniques.

PMB is slower than sandblasting, yet faster than chemical stripping on flat simple surfaces. PMB is faster and more efficient on complex surfaces where hand sanding must be used. PMB can be considered a technically and economically viable alternative paint stripping process for many paint removal requirements. Although this study was conducted at a military maintenance installation, the conclusions derived should be consistent in the private industrial sector.

TABLE 5. METRIC CONVERSION TABLE

Nonmetric	Times	Yields Metric
ft^2	0.09	m^2
gal.	3.79	L
lb	0.454	kg
psi	6.89	kPa

HAZARDOUS WASTE RESEARCH PERTAINING TO METAL FINISHING

by

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NOTICE

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HAZARDOUS WASTE RESEARCH PERTAINING TO METAL FINISHING

by Clyde J. Dial

Options for waste management are changing rapidly in the United States. This is true for any industry that produces a hazardous waste. Your industry is no exception. The Environmental Protection Agency (EPA) has conducted research to evaluate or develop metal waste control techniques for a number of years. This paper presents a brief description of the most important projects that have been conducted since 1978. These projects include efforts of the programs that are conducted not only by the Alternative Technologies Division of the Hazardous Waste Engineering Research Laboratory but also those managed by Roger Wilmoth, Chief of the Manufacturing and Service Industries Branch of the Water Engineering Research Laboratory. Within EPA's research program, these two Laboratories manage all of the engineering research activities of the Agency that deal with hazardous metallic wastes. Work has centered on assessment of the problems and evaluation and development of control techniques or technologies.

Our preference for the management of any waste stream is represented by the following hierarchy:

- Waste elimination,
- Recycle,
- Reuse,
- Burn as fuel,
- Incineration,
- Chemical/biological detoxification,
- Volume reduction, and
- Solidify and dispose.

The current research program is focused on two broad objectives--first, to do performance evaluations of existing treatment technology/waste stream combinations to determine the best demonstrated available technology (BDAT) for that waste stream and, secondly, to explore new concepts that can provide additional options for the control of metals. Work performed by the Office of Solid Waste is providing the analysis from which the technology assessment plan is developed. This report[1] provides an evaluation of the sources and extent of cyanide and metal-bearing hazardous wastes and an analysis of current management practices for treating or disposing of these wastes. It includes an examination of the costs of current practices and the residuals and the emissions from treatment systems. From the 1983 study, the nationwide generation rate of metal-bearing wastes was 7.9 billion gallons per year. The rate of generation of cyanide metal-bearing wastes was 4.7 billion gallons per year, and the estimated rate of generation of reactive wastes containing cyanides was 0.8 billion gallons per year. The greatest number of waste-generating facilities studied was related to the plating and polishing, paints and allied products, metal coatings and allied products, motor vehicle parts and accessories, and industrial inorganic chemical industries. Wastes handled by treatment, storage and disposal facilities amounted to 5.8 billion gallons of metal-bearing wastes, 3.3 billion gallons of cyanide-bearing wastes, and 0.76 billion gallons of reactive wastes reported as cyanide bearing. Nearly a fourth of all of these wastes were land disposed, and approximately 85 percent of those wastes were aqueous. The most common method for land disposal was deep-well injection. Treatment schemes were identified which will chemically or physically fix these wastes such that their solubility or leachability is well within the California-ban criteria and the EP toxicity criteria.

The Agency's approach to managing hazardous wastes will be to require that the waste stream, after treatment, passes three tests before it may be land disposed. The first test is the "paint filter" test. This is a simple test to ensure that the waste does not contain free moisture prior to placing it in a land disposal operation.

The second test concerns the landfill restriction or BDAT number. For each hazardous component that may be present in a particular listed waste, EPA will establish maximum concentrations that are permissible in order for that waste to be disposed to the land. This maximum concentration will be based on protection of human health and the environment or will represent the lowest concentration that can be achieved through treatment with the BDAT. Work, which will be described shortly, centers on producing these numbers for the Agency.

The third test that must be passed is the proposed toxicity characteristics leaching procedure (TCLP). This TCLP contains a health-based limit for some 54 compounds, including 9 metals. If the leachate found through the TCLP contains concentrations of the TCLP listed compounds in excess of the limits established for the TCLP, the waste must be treated until the waste passes the TCLP.

In order to establish the BDAT, a matrix of control technology processes for waste streams containing metals and cyanides has been developed. The control technology processes under consideration are incineration, sulfate precipitation, alkaline chlorination, chromate reduction, sulfide precipitation, lime precipitation, and solidification/stabilization. For each of these processes, engineering judgment will be used to determine what is considered to be the best treatment train for those metal and cyanide wastes that are being controlled by the Agency under RCRA. There are 66 such wastes. They include five categories:

- D - Wastes because they exhibit a specific characteristic,
- F - Non-specific wastes, regardless of source,
- K - Wastes from specific operations,
- P - Acutely hazardous commercial products or process intermediates, and
- U - Specific commercial products that are toxic.

X4

After having determined what is believed to be the best treatment scheme, actual performance evaluations to demonstrate the type of treatment capability that exists for that waste stream will be conducted. These demonstrations will be done in one of three ways. Actual visits to a facility that is using that treatment scheme for a particular waste will be made, and full-scale performance evaluations of that system will be done. In other cases, mobile pilot-scale equipment will be taken to a field site to use a slip-stream from that facility to demonstrate the treatment capability at pilot scale. Treatment capabilities will also be demonstrated by bringing a particular waste to the Test and Evaluation Facility in Cincinnati to test at pilot scale. As one might suspect, each individual waste stream will not be tested, primarily for two reasons. First, in practice, some of these waste streams are rarely separated from others. Secondly, a number of the waste streams has characteristics almost identical to others, and in those cases, tests of one of the waste streams will be done to demonstrate treatment capability for each of the waste streams in that group having common characteristics.

The evaluation program is under way. So far, performance evaluations have been conducted for the sites listed in Table 1. Because these performance evaluations have just recently been completed, the results of this work are not yet available. This information and information on further planned tests will be available for use on a continuous basis in about two months. It is important to note that the cooperation of industry with the EPA in the conduct of this performance evaluation program has been quite good. This cooperative spirit between the industry and ourselves is essential in order to arrive at the most common sense decisions regarding the management of these metal-bearing wastes.

Currently, two projects that are under way could lead to new techniques to selectively remove metal from waste streams. The first is actually a continuation of the metal recovery program at Montana Tech. This research is aimed at improving the iron removal step of the process. The initial recovery process precipitated the iron as a jarosite, a complex mineral containing iron, potassium, sulfur, oxygen and hydrogen. Although the jarosite forms an easily filterable precipitate, it has the disadvantage of carrying down other cations into its crystalline matrix. Since some of these are toxic heavy metal ions whose concentrations are above those allowed by the RCRA reauthorization, we have had to take a different approach to iron removal.

The current project is based on chemistry whereby the copper is removed first by cementation on iron powder (in previous work copper was removed by solvent extraction after jarosite precipitation) and then iron is precipitated with phosphoric acid. The phosphate thus formed is even easier to filter than the jarosite, and after the iron is precipitated, heating the solution to about 80° Celsius precipitates chromium as the phosphate. This application of phosphate precipitation will be tested to recover metals from mixed metal sludges such as those from plating wastes and electrochemical machining.

A second potentially valuable program is evaluation of compounds which can selectively remove metal from aqueous streams. This effort is the first

TABLE 1

TEST SUMMARIES

LANDFILL BAN PERFORMANCE EVALUATION PROGRAM

SITES TESTED

Waste Codes	Waste Composition	Waste Source	Treatment Technology	Principal Performance Parameters
D002 Spent Nitric Acids and Metals	38% Nitric Acid (E) 5-10% Copper (E) <0.1% Organics (E) 50+% Water (E)	Electronics (Printed Circuit Board Manufacturing)	Neut./Lime Addition/ Precipitation/ Centrifugation/ Reclaimed Metal	Metals, VOC's, pH, TOC, EP tox., TCLP, Paint Filter
D002, D004 Mixed Aqueous Metal-Laden	2% Arsenic (E) 25% Nitric Acid (E) 3% HF (E) 70% Water (E)	Aerospace, Auto Manufacturing	Chemical Coag./ Precipitation/ Sedimentation/ Evaporation/ Carbon Adsorption	TOC, Metals, VOC's, EP tox.
D002, D007, F006 Waste Paint Sludge, Waste Plating Sludge, Cleaning Solution	Paint Sludge (E) Zinc Phos. Sludge (E) Biopond Sludge (E) Metal Sludge (E)	Auto Manufacturing Petroleum Air Force Base	Solidification w/Fly Ash	Paint Filter, EP tox., TCLP
D002 Mixed Aqueous Metal-Laden	<5% Metals (E) <0.1% Organics (E) 95% Water (E) Trace CN (E)	Electrical Components, Applicance Manufacturing	Lime Addition/ Precipitation/ Filtration/ Carbon Adsorption	Metals, VOC's, TOC, EP tox., Cyanide, COD
F007 Cyanide Rinse	<0.5% Metals (E) 500 ppm CN (E) 99% Water (E)	Plating	Cyanide Dest. (alkaline chlorination followed by aqueous waste treatment)	Metals, TOC, CN, VOC's

attempt to use the chemical process that living cells possess that enables them to capture and transfer metals. Their chemical ligands are being synthetically produced for these experiments. Such compositions have, in laboratory demonstrations, removed copper, nickel, and other toxic heavy metals, while letting innocuous ions such as calcium, sodium, etc., pass through. If pilot studies on mixed waste streams, such as leachate from landfills or plating rinse waters are successful, we intend to continue this effort at a larger scale. Our efforts will center on four tasks:

(1) Determine amount of metals removed per gram of compound,

(2) Number of regenerations compound can undergo,

(3) Scale-up so that design and cost estimates may be made (8 to 10 gpm pilot plant), and

(4) Determine effects of organic contaminants on metal removal efficiency.

PAST RESEARCH PROJECTS[2]

The Environmental Protection Agency has sponsored research into metal removal and/or recovery from wastewaters and sludges for over ten years. Early efforts concentrated on precipitating metals to protect waters but the wisdom of also reclaiming metal was soon recognized as a means of reducing water pollution while conserving metal/resources. Work done for EPA at Battelle Columbus in 1975 included a survey of plating facilities and the volume and types of metals discarded in sludges. As understanding of the problem began to develop, a series of investigations was funded, each adding to the overall bank of information. These projects are listed in reverse chronology below.

Metal Value Recovery from Metal Hydroxide Sludges[3]

The latest EPA projects were undertaken at the Montana College of Mineral Science and Technology (Montana Tech) and tied together much of the previous work. The first phase of the investigation was a carefully executed series of laboratory experiments to establish the processes needed to leach hydroxide sludges (the most plentiful type produced by electroplating EP Shops) with sulfuric acid, and the various recovery methods required for copper, zinc, chromium, and nickel. Flowsheets were constructed and the unit operations required to make a complete recovery process were developed.

In phase two, a pilot assembly capable of processing 75-100 lbs. of sludge per day was built and operated at a large electroplating facility. While not entirely troublefree, the operation was smooth enough to allow confirmation of the possible commercial viability of the process, and development of a computerized mass balance.

The steps of the process were as follows.

- The sludge is leached with sulfuric acid.

- Iron, which is frequently present in EP sludges, was removed by precipitating as a potassium jarosite [$KFe_3(SO_4)_2(OH)_6$]. This must be done first, as iron interferes in many of the subsequent recovery steps. This step is in need of improvement, because in the process of precipitating the jarosite some anions such as chromate are removed, along with some heavy metal cations. Even though the volume of the jarosite sludge is much less than that of the starting material, the waste would be classed as hazardous, requiring special precautions and extra costs when landfilling. Because of these faults, it is proposed that a new program be instituted to attempt to remove iron without the inclusion of large amounts of other heavy metals.

- Conventional techniques were used to extract copper from the acid solution using an oxime in petroleum solvent. The copper was then stripped from the organic phase with stronger acid and electrowon or crystallized as sulfate.

- Zinc and cadmium were extracted with diethyl hexyl phosphoric acid (D_2EHPA), leaving chromium and nickel behind. Again, a sulfuric acid strip was used for zinc removal from the organic phase. Small amounts of residual iron are removed in early stages of extraction; ten extraction stages are required to remove iron-free zinc.

- Chromium was oxidized to Cr^{+6} with chlorine, then selectively precipitated as lead chromate which can be sold as a pigment or regenerated to chromic acid with sulfuric acid. The lead sulfate precipitate formed when chromic acid is regenerated may itself be recycled to precipitate more lead chromate. In some instances SO_2/O_2 oxidation of the chromium may be more desirable.

- Nickel is precipitated as sulfide, the only heavy metal in the process which is not directly recyclable back to a plating operation. However, several alternative techniques are presented to yield a nickel ammine, or nickel sulfate may be solvent extracted with a mixture of chelating agents.

Recognizing that some improvements could be made in the various separation steps, first order cost estimates indicate that a 50-ton per day recovery plant could not only reduce landfill volume considerably, with consequent less chance of pollution, but in addition could yield a profit as shown in Table 2.

Metal Recovery from Electrochemical Machining and Electrodischarge Machining (ECM/EDM) Wastes[4]

These relatively new machining processes produce heavy metal wastes; ECM yields hydroxide sludges heavily contaminated with sodium chloride, and EDM finely divided particles of the alloy being machined. Both ECM and EDM are primarily used on hard alloys, often high in nickel, chromium, cobalt, molybdenum, etc. This project involved a survey of ECM/EDM shops, the volumes of sludge

TABLE 2

PROCESS COST: FIRST ORDER ESTIMATE

UNIT OPERATION	COST ($)*			
	Factored Capital Cost Estimate	Annualized Capital Cost	Operation Cost Per Year	Total Cost Per Year
1. Leach, jarosite precipitation	430,800	119,500	223,500	343,000
2. Jarosite storage	390,500	108,200	25,400	133,600
3. Copper solvent extraction, electro-winning	336,100	93,100	205,900	299,000
4. Zinc, residual iron solvent extraction, zinc sulfate crystallization	661,600	183,300	269,700	453,000
5. Chromium oxid., chromic acid production	1,818,200	503,600	407,700	911,300
6. Nickel recovery	231,600	64,200	230,000	294,200
TOTAL COST	3,868,800	1,071,900	1,362,200	2,434,100
Profit (Gross)			1,071,900	

*Assuming a $1.00 per gallon credit for sludge from producers.

produced, metal content, and disposal practices and costs. Several recovery routes were studied, including the procedures outlined above.

Cadmium Recovery from Electroplating Wastes[5]

This project was primarily concerned with methods and costs for recovering cadmium from plating shops which are able to segregate Cd from other sludges, or perhaps those whose only business is cadmium plating. The authors give very little thought to the fact that many platers use cadmium at least occasionally, and do not segregate their sludges. The recovery technique (melt and/or distill cadmium electromotively displaced with zinc metal) is most effective on low chromium and nickel sludges. While chromium is not displaced by zinc, nickel would have to be removed by distilling the zinc.

Coupled Transport Systems for Control of Heavy Metal Pollutants[6]

Coupled transport membranes are made by immersing a microporous membrane into a liquid complexing agent such as those used for liquid/liquid extraction of metals from solution. The liquid (often called a liquid ion exchanger) then acts as a transfer agent to move metal ions through the capillaries, using the driving force of the pH gradient across a membrane separating an acidic from a basic solution. Data are presented which suggest that a membrane unit having 450 to 500 square feet of surface could separate chromium from the rinse water of a medium sized plating line. The separation unit would cost about $5,000, compared to over $50,000 for an evaporative-ion exchange system.

Evaporative Recovery of Chromium Plating Rinse Waters[7]

A demonstration of this process was given by Advance Plating Company, Cleveland, Ohio on the first of four counterflow rinse tanks. After first passing through a cation exchanger to remove metallic impurities, water from the first rinse tank is drawn into a vacuum evaporator, whose condensate is returned to the third rinse tank. Concentrated acid produced in the evaporator bottoms is returned to the plating bath. The value of recovered chrome has enabled the operator to pay off the equipment in two years or less, in addition, the chromic acid in dragout water is reduced by 99.98%.

Removal of Toxic Metals from Metal Finishing Wastewater by Solvent Extraction[8]

This short investigation of solvent extraction was primarily limited to one extraction agent, Alamine 336 (General Mills). By increasing acidity stepwise with HCl, selective removal of chromium, cadmium, and zinc from wastewaters was demonstrated. Copper and nickel could not be extracted with this reagent; several other high molecular weight amines were tried without success.

Reverse Osmosis Field Test: Treatment of Watts Nickel Rinse Waters[9]

Rinse waters from a Watts type (primarily nickel sulfate) nickel plating operation were passed through a polyamide membrane, effectively separating a concentrated nickel salt solution and recycling the rinse water. Results were very encouraging, indicating that the capital cost of the R.O. unit could be recovered in about a year, based on the reduction in water usage plus metal values returned to the plating bath. This process could be more accurately described as recycling or conservation since there is no chemical change of metals recycled to the bath.

Treatment of Metal Finishing Wastes by Sulfide Precipitation[10,11,12,13]

Although the process of sulfide precipitation has been known for many years, its use as a means of pollution control appears to be of fairly recent origin, and, is mentioned here primarily to illustrate an effective method of metal removal. A major disadvantage of sulfide precipitation is the lack of selectivity; it is apparently impossible to precipitate a single metal without major contamination by other metal sulfides. Use of a polymeric flocculant (preferably anionic) increased the settling rate, and adding a chelating agent such as EDTA (ethylenediamine tetraacetic) acid at the proper pH greatly aided selectivity.

Heavy metal sulfides, even if effectively separated, are extremely difficult to reduce to their corresponding metals by hydrometallurgical methods, and are generally recovered by smelting. The large volumes of raw material required to support such smelters makes plating waste metal recovery by this method impractical.

A Reclamation of Metal Values from Metal Finishing Waste Treatment Sludges[14]

A survey of plating opertions involving over 600 questionnaires (150 replies) revealed the extent of sludges generated by the industry, and even developed a "typical" analysis of metal content; the copper, nickel, and chromium contents were very similar to those found in subsequent studies. Some preliminary laboratory leaching and extraction studies led to the conclusion that metal recovery could be economically feasible only if the process could be carried out on a large, and preferably continuous scale. Based on then current (1971) metal prices, it was concluded that chromium and zinc recovery were uneconomic; the writers apparently did not foresee the ban on landfilling of heavy metal wastes now being implemented.[12] The only laboratory work done by these investigators were leaching experiments with ammonium carbonate and sulfuric acid which indicated that acid leaches were adequate for most hydroxide sludges while ammonium carbonate would only dissolve copper and nickel. A literature study of several potential recovery methods for copper and nickel was made, but no work was done to verify their efficacy; again, chromium recovery was not considered.

REFERENCES

1. Versar, Inc., Preliminary Draft Report, "Technical Assessment of Treatment Alternatives for Wastes Containing Metals and/or Cyanides," EPA Contract No. 68-03-3149, Work Assignment No. 15-5, Versar Project No. 817.3, October 1984.

2. Howell, S. Garry, "EPA Research to Recover Toxic Heavy Metals from Waste Streams," Proceedings from the 11th Annual Research Symposium on Incineration and Treatment of Hazardous Waste, Cincinnati, Ohio, April 1985.

3. Twidwell, L. G., "Metal Value Recovery from Metal Hydroxide Sludges," report in preparation.

4. Holcombe, L. J., et al., "Metal Recovery from Electrochemical Machining and Electrical Discharge Machining Wastes," report in preparation.

5. Lloyd, T. B.; Wise, K. J., "Cadmium Recovery from Electroplating Wastes," unpublished EPA report.

6. Babcock, W. C., et al., "Coupled Transport Systems for Removal of Heavy Metal Pollutants," EPA 600/2-79-181.

7. Advance Plating Company, "Evaporative Recovery of Chromium Plating Rinse Waters," EPA 600/2-78-127.

8. McDonald, C. W., "Removal of Toxic Metals from Metal Finishing Wastewater by Solvent Extraction," EPA 600/2-78-011.

9. McNutty, K. J., et al., "Reverse Osmosis Field Test: Treatment of Watts Nickel Rinse Waters," EPA 600/2-77-039.

10. Schlauch, R. M.; Epstein, A. C., "Treatment of Metal Finishing Wastes by Sulfide Precipitation," EPA 600/2-77-049.

11. Wilson, D. L., "Control and Treatment Technology for the Metal Finishing Industry: Sulfide Precipitation," EPA 625/8-80-003.

12. Robinson, A. K.; Sum, J. C., "Sulfide Precipitation of Heavy Metals," EPA 600/2-80-139.

13. Bhattacharyya, D.; Chen, L. F., "Sulfide Precipitation of Nickel and Other Heavy Metals," 3-volume unpublished EPA report.

14. Tripler, A. B., et al., "Reclamation of Metal Values from Metal Finishing Waste Treatment Sludges," EPA 670/2-75-018.